

VIABILITY OF CO-PROCESSING OF COAL, OIL AND WASTE PLASTICS

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INTRODUCTION

The disposal of wastes represents not only a significant cost but also concerns such as loss of a valuable resource, a health hazard, and pollution resulting from conventional disposal methods, such as landfilling and incineration. Through the efforts of the U.S. Department of Energy and Hydrocarbon Technologies, Inc(HTI), a novel process, HTI CoPro Plus™, has been developed to produce alternative fuels and chemicals from combined liquefaction of waste plastics with coal and heavy petroleum residues. The new process concept that has been successfully tested in HTI strives to:

- Direct organic waste away from landfills.
- Produce valuable products, basic and intermediate chemicals and fuels.
- Solve existing environmental problems created by current disposal methods.
- Reduce refinery waste oil pond and land fill inventories.
- Enhance domestic resources by
 - Supplanting oil and fuel supply imports.
 - Reducing energy consumption through recycling.
 - Improving the trade balance.
 - Creating a new industry and U.S. jobs.

With the rapid decreasing in availability of landfills but nationwide increasing in waste plastics generation, co-processing is a viable option for addressing this environmental problem. Economical evaluation has shown that co-processing of plastics with oil, coal or their mixture reduced the equivalent crude oil price to a compatible level.

The new approaches involve continuous pilot plant operation utilizing finely dispersed catalyst (HTI Gel Cat™) to simultaneously liquefy the solid feed and upgrade residuum from either liquefied solid or petroleum oil to lower boiling (<524°C) premium products. The HTI GelCat™ has a high surface area exceeding 100 m²/g in dried form and has particle size smaller than about 50 Angstrom units. Because the fine-sized catalyst are produced based on use of available relative inexpensive material and since the principal component is cheap and environmentally benign, they are usually disposable for large scale process and do not require recovery and regeneration.

This paper discusses the results from several successful pilot tests of DOE's POC program performed in HTI. Different waste materials, such as MSW plastics, auto-sluff, Hondo VTB resid, were co-processed with coal directly, or pretreated by pyrolysis prior to co-processing with coal. Apart from exploring HTI Gel Cat™ catalyst, integrated reactor configurations including interstage separator, in-line hydrotreating and combination of dispersed and supported catalyst system have been evaluated during these pilot tests. One significant characteristics of HTI's CoPro Plus™ is the increase in hydrogen efficiency as both hydrogen consumption and C₁-C₃ gas yield decrease. Promising process performance, in terms of high distillate yield and extensive removal of heteroatoms, has been demonstrated through HTI's new approaches.

PROCESS DESCRIPTION

The HTI CoPro Plus process entails co-liquefaction of organic wastes with coal and/or oil is a liquid phase hydrogenation process that takes place at temperatures of about 425°C and pressures of 15 MPa. Under these conditions, large molecules are cracked, hydrogen is added and sulfur, nitrogen, and chlorine, etc. are easily separated and recovered after conversion to their basic hydrogenated form. Also, because the process is contained under pressure, all gases and inert components can be captured and reused if desired. Co-liquefaction of random waste organic materials with coal provides for the efficient recovery and recycle of problem wastes back into the economy as premium transportation fuels and feedstocks for virgin plastics. Direct liquefaction is also applicable to the conversion and liquefaction of densified solids refuse derived fuels (RDF), formed from municipal and industrial wastes and automobile shredder residue (ASR). On a conversion to transportation fuel basis the recycle and conversion of waste plastics, waste oils, tires and organic wastes with only 50% of the waste being recovered shows that this process can supplement 10% of the United States' daily transportation fuel requirements:

<u>Waste Type</u>	<u>Quantity Per Year</u>	<u>Oil Equivalent</u> Million Barrels/Year
Plastics	3.5 Million Tons	200
Used Waste Oil	1.4 Billion Gallons	33
Rubber Tires	350 Million PTE*	8
Other Organic	34.4 Million Tons	<u>212</u>
Total Waste		453
Total Coal/Waste (1:1)		906
Total at 50% Waste		453+

*Passenger Tire Equivalents

+About 10% of daily U.S. Transportation Fuel Use

A techno-economic analysis for a site specific waste/coal direct liquefaction plant at 12,000 bbls/day adjacent to and integrated with an oil refinery with random waste delivered to the plant shows an average required selling price at zero acquisition cost and at 15% ROI of about \$16.00 per barrel. If tipping fees are included and if high value plastic feedstocks are recovered, the price could be less than \$14/bbl and is cost effective today. This selling price will be in the competitive range by the end of this century, even with a +\$20/ton acquisition cost, particularly if the environmental cost benefits of recycling are included. The current national average tipping fee is \$28/ton for landfilling and \$54/ton for incineration.

EXPERIMENTAL

Pilot scale tests were carried out at HTI using a 25 Kg/h two-stage pilot plant. The coal, oil, waste materials and HTI Gel Cat™ catalyst were premixed in a mixing tank prior to charging to the Feed Tank. Joined by feed hydrogen, the gas/feed slurry stream passed through a short residence time coiled preheater. Reaction was conducted at 15MPa of hydrogen, 400-460°C and 1000-5000 ppm of Fe catalyst loading. An internal circulating pump returned a portion of the reactor slurry to the bottom of the reactor providing the backmixing action. The first stage light reaction product was cooled and separated from the main slurry. This light product, along with other second stage non-hydrotreated products, were fed to the direct-coupled hydrotreater. The intermediate slurry product was further liquefied in the second stage backmixed reactor.

The hot vapor products from the second stage liquefaction reactor were separated in the hot separator and fed directly into a fixed bed hydrotreater. The hydrotreater was connected directly with the hot separator without pressure reduction. Hydrogen, C₁-C₃ hydrocarbons, heteroatom gaseous products, water and volatile liquid products from the overhead of the separator passed through a mixing phase trickled bed hydrotreater. The main function of the hydrotreater was to stabilize the hydrocarbon products and to reduce heteroatom (N,S,and O) content.

The backend separation included pressure filtration and batch vacuum distillation. The major net product streams are product gases (1st and 2nd stages), dissolved gas (2nd stage only), 2nd stage separator overheads (hydrotreated product) and toluene extracted solids and excess pressure filter liquid (PFL) or vacuum still overhead (VSOH). Process performance is determined by feed composition, operating conditions, yield and quality of C₄-524°C distillate, and by hydrogen utilization efficiency.

RESULTS AND DISCUSSION

The process performance and economic evaluation obtained from recent pilot scale co-processing operations are summarized in this paper. The economic evaluation studies were based on construction of a fully-integrated grass-roots commercial coal/oil/waste (plastics) co-liquefaction complex to manufacture finished gasoline and diesel fuel liquid products. 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 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. 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. 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.

Table 1 presents the comparisons of the performance of five run conditions. Coprocessing of Black Thunder coal, Hondo oil and ASR resulted in 83.6 W% resid conversion and 66.8 W% distillate yield. A dramatic drop in both resid conversion and distillate yield was observed when Hondo oil was removed from the mixture of coal and ASR(PB-04-4). It seemed that vehicle solvent is essential in converting ASR and coal. In Run PB-04-5, 25 W% of plastics was added to the coal and ASR mixture, it is interesting to note that distillate yield was increased from 56.6 to 61.4 W% while 524°C+ resid conversion was increased proportionally, from 72.4 to 77.2 W%. Also, it is observed that addition of plastics has a significant impact on hydrogen consumption. Not only does the addition of plastics to coal/ASR improved the process performance it also decreased hydrogen consumption by about 2 W%. Economical analysis showed that by adding plastics to coal/ASR feedstock, equivalent crude oil price dropped by \$6/barrel.

It was concluded that auto-fluff, that contains primarily polyurethanes and high impact polystyrene as its principal polymeric constituents, was not as effective as the MSW plastics in improving the coal hydroconversion process performance, i.e. auto-fluff was not found to either increase the light distillate yields or decrease the light gas make and chemical hydrogen consumption in coal liquefaction, in the manner done by MSW plastics

In Run PB-06, waste plastics was pretreated by pyrolysis and only 343 °C+ pyrolysis oil was coprocessed with coal and Hondo oil. As shown in *Table 1*, Run PB-06-3, performance of coprocessing of coal/Pyrolysis oil, in terms of distillate yield and resid conversion, was similar to coprocessing of coal/ASR (PB-04-4), slightly decrease in hydrogen consumption was observed. Considering Mo catalyst was not used in Run PB-06-03, this result seemed to suggest that pyrolysis oil was more reactive in improving coal conversion than ASR. Run PB-06-4, using a mixed feed of coal, Hondo oil and pyrolysis oil, was performed at higher space velocity. Distillate yield and 524°C+ resid conversion was decreased by 3 and 7 W%, respectively. However, C₁-C₃ light gas yield and hydrogen consumption decreased significantly.

Result from Run PB-06-4 demonstrated the potential for commercialization because the equivalent crude price dropped to \$ 19.6/barrel.

Table 2 illustrated the comparison of co-processing performance using different coals. In comparing the same feed mixture, Illinois #6 coal (Run PB-05-4) appeared to be more reactive than Black Thunder coal (Run PB-06-2), as both the distillate yield and resid conversion were higher. However, the use of Illinois #6 coal resulted in higher hydrogen consumption under the same conditions. Significant improvement were obtained in co-processing of Illinois #6 coal, Hondo oil and plastics (PB-05-3).

The liquid products from these co-processing operations were clean and good feedstocks for the refining operations, including hydrotreating, reforming, and hydrocracking. For these distillates, heteroatoms could be easily reduced- if needed, also, better FCC gasoline yields require less hydrocracking capacity for coal liquids than petroleum. These distillates made acceptable blendstock for diesel and jet fuel, due to their high cetane number (42-46) and high naphthenes (over 50 v%) content. The superior quality of distillate products from HTI's coprocessing runs (attributable to HTI's in-line hydrotreating operation) was found to fetch a three-dollar premium over the neat petroleum liquids.

CONCLUSIONS

The new dispersed catalyst, developed by HTI, GelCat™, has been very effective for co-processing of coal, plastics and other organic waste material. Excellent process performance in terms of carbonaceous feed conversion to liquid and gaseous products, light distillate yields, and hydrogen consumption have been obtained during the co-processing of different types of feed materials including coal, heavy petroleum resid, municipal solid waste plastics, and auto-fluff. The addition of waste plastics, or pyrolysis oil, from plastics to the feed increase hydrogen efficiency as both hydrogen consumption and C₁-C₃ light gas yield decrease. The co-processing of coal, oil and plastics has achieved an extremely low equivalent crude oil price of \$19.64/barrel, putting it nearly in the range of economically commercializing.

Table 1: Performance Comparison-Yields(Black Thunder Coal)					
Run ID	PB-04-3	PB-04-4	PB-04-5	PB-06-3	PB-06-4
Feed Comp.W%	Coal/Oil/ASR	Coal/ASR	Coal/ASR/PLS	Coal/Pyr. Oil	Coal/Oil/Pyr
Coal	50	75	50	67	45
(Black Thunder)					
Hondo Oil	30				28
Plastics			25		
ASR	20	25	25		
343°C+ Pyr. Oil				33	27
Catalyst					
Fe/P	1000	1000	1000	1000	1000
Mo	50	50	50	0	0
Space Velocity					
(kg/h/m ³)	602	632	621	655	1356
Performance					
(W% maf feed)					
Conversion	94.1	90.5	91.3	91	86
C ₄ -524°C Yield	66.8	56.6	61.4	57	54
524°C+ Conv.	83.6	72.4	77.2	73	66
C ₁ -C ₃ Gas Yield	8.6	6.9	7.8	8.8	3.5
H ₂ Consumption	5.7	6.0	4.0	5.4	2.2
Economic Comparison (12,000 Tons/Day Total Feed)					
Feed Rate, T/D					
Coal	6000	9000	6000	8040	5400
Hondo Oil	3600				3360
Plastics			3000		
ASR	2400	3000	3000		
343°C+ Pyr Oil				3960	3240
Liquid Prod, B/D					
Gasoline	13196	10141	12205	11527	10310
Diesel Fuel	32048	24629	29641	41238	35875
Total Investment					
(\$MM)	2680	2654	2644	2734	2852
Operating Cost					
(\$MM/Yr)	583.6	519.5	561.9	505.2	639.9
Eq. Crude Oil,\$/b	30.34	36.25	28.99	23.41	19.64

ASR=Auto Shredder Residue

PLS=Plastics

Pyr Oil=Pyrolysis Oil

Table 2: Performance Comparison-Yields(Black Thunder vs Illinois#6 Coal)					
Run ID Feed Comp.W%	PB-04-5 Coal/ASR/PLS	PB-06-2 Coal/PLS	PB-05-3 Coal/Oil/PLS	PB-05-4 Coal/PLS	PB-05-5 Coal/ASR/PLS
Coal (Black Thunder)	50	67			
Coal (Illinois # 6)			33	67	67
Hondo Oil			33		
Plastics	25	33	33	33	17
ASR	25				16
343°C+ Pyr. Oil					
Catalyst					
Fe/P	1000	1000	1000	1000	1000
Mo	50	0	50	50	50
Space Velocity (kg/h/m³)	621	560	579	669	758
Performance (W% maf feed)					
Conversion	91.3	91	99.1	97.1	96.2
C ₄ -524°C Yield	61.4	59	78.8	74.6	72.4
524°C+ Conv.	77.2	75	89.6	84.3	81.6
C ₁ -C ₃ Gas Yield	7.8	7.9	9.0	8.2	7.1
H ₂ Consumption	4.0	3.9	3.9	5.4	5.8
Economic Comparison (12,000 Tons/Day Total Feed)					
Feed Rate, T/D					
Coal	6000	8040	4000	8040	8040
Hondo Oil			4000		
Plastics	3000	3960	4000	3960	2040
ASR	3000				1920
343°C+ Pyr Oil					
Liquid Prod, B/D					
Gasoline	12205	12305	16201	14354	13645
Diesel Fuel	29641	29885	39346	34860	33137
Total Investment (\$MM)	2644	2469	2450	2449	2551
Operating Cost (\$MM/Yr)	561.9	446	514.3	486.3	515.9
Eq. Crude Oil,\$/b	28.99	26.19	22.43	24.20	25.20