

THE DIRECT LIQUEFACTION CO-PROCESSING OF COAL, OIL, PLASTICS, MSW, AND BIOMASS

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2. Liquefaction
3. Direct

ABSTRACT

Hydrocarbon Technologies, Inc. (HTI) and the United States Department of Energy (DOE) have been working on the application of the Direct Liquefaction Process to the conversion of various low-cost, carbon-based feedstocks. In the United States, direct liquefaction has been directed to utilize waste and biomass in combination with coal and oil in order to lower CO₂ emissions and to be cost-competitive. Through collaboration with DOE, HTI has become our country's leading R&D and commercial developer of Direct Liquefaction. Under a current DOE contract, HTI has developed waste plastics/coal co-processing technology to produce fuels that can be produced at a cost comparable to crude oil. Further development would reuse/recycle plastics and waste organics, turn them into valuable feedstocks, remove sulfur and nitrogen, and lower CO₂ emissions, while utilizing domestic feedstocks.

Conversion and yield data will be presented for various feedstock combinations and concepts presented for further studies. The economics of coal and waste co-processing will be forecast based on stand-alone and refinery-integrated facilities.

INTRODUCTION

Direct Liquefaction involves the addition of hydrogen to unsaturated hydrocarbons, followed by rearrangement, cracking of bulky molecules, and removal of heteroatoms to produce lighter and cleaner transportation fuels (gasoline, diesel, and jet) and specialty chemicals and carbon-based products. In the process, the sulfur and nitrogen are removed by reduction and conversion to sulfur and ammonia.

With Direct Liquefaction, fuels are produced in a process similar to the hydrocracking of heavy oils in today's refineries. Hydrogen is added to the carbon chain, heteroatoms are removed, and the larger molecules are cracked and rehydrated to clean fuel molecules at energy efficiencies over 75 percent. In Indirect Liquefaction, fuels and chemicals are constructed from single carbon structures (syngas) produced by gasification into higher molecular weight fuels by Fischer-Tropsch Chemistry and additional processing at overall energy efficiencies approaching 50 percent. Thus, Direct Liquefaction is a more efficient process with lower emissions.

The Direct Liquefaction process for coal and coal/oil/plastics feedstocks has been under development for over 30 years under the auspices of the United States Department of Energy and its predecessors as constituted today. It is an extremely versatile, highly efficient process that can convert nearly all low-cost carbon-based feedstocks into fuels and chemicals. According to the "vision" of the DOE, by the year 2015, large fractions of municipal, agricultural, and industrial wastes will become valuable energy resources. These currently wasted resources can be recovered and recycled in economical and environmentally sound ways through development of co-processing technologies using our abundant fossil fuel resources.

Recently, the technology has been directed to utilize waste plastics and other waste hydrocarbons in combination with coal and heavy oils in order to address waste disposal issues, lower CO₂ contribution emissions, and be more cost-competitive. Through collaboration with DOE and Industry, HTI has developed waste plastics/coal/oil co-processing technology that can produce fuels at a projected cost comparable to crude oil at \$16/barrel. This development would reuse/recycle plastics, turn them into valuable feedstocks, lower emissions, and utilize domestic feedstocks and waste materials to supplement imported oil.

Hydrocarbon Technologies is continuing to direct its R&D activities towards the development of a Renewable Energy Clean Fuels Complex of the future utilizing the energy efficient Direct Liquefaction Process for the production of clean transportation fuels, chemicals, and carbon

products. The HTI CoPro Plus™ process entails co-liquefaction of organic feedstocks with coal and/or oil in a two-stage reactor system using a dispersed catalyst and in-line hydrotreating.

Process Equipment Description

The coal/oil slurry is premixed off-line and charged to a feed tank on a periodic basis. The slurry feed is pumped through both reactors with or without interstage separation. Interstage separation, if used, removes the light oils and the gases from the first reactor so that the second reactor is more efficiently used to upgrade only the remaining heavy material. The effluent from the second reactor is separated in a hot separator. The overhead from the hot separator is sent to a cold separator and separated into a vent gas stream and a separator overhead stream (SOH). The vent gases are metered, sampled, and sent to flare, and the SOH is collected. The second stage hot separator overhead stream can also be sent directly to an in-line hydrotreater for further upgrading and heteroatom removal. For co-processing and heavy oil upgrading, the bottoms material from the hot separator is separated off-line in a batch vacuum distillation into a vacuum still overhead stream (VSOH) and a vacuum still bottoms stream (VSB). These streams are then analyzed. Part of the VSOH is used as a process oil in the buffer pumps for the first and second stage reactors. For coal liquefaction, the bottoms material from the hot separator is separated off-line in a pressure filter into a pressure filter liquid (PFL) and a pressure filter solid (PFS). These streams are then analyzed. Part of the PFL is used as a process oil in the buffer pumps for the first and second stage reactors, and part of the PFL is used as slurry oil for the coal and fed back to the reactors. Figure 1 shows a schematic of the process.

EXPERIMENTAL RESULTS

Throughout the co-liquefaction programs at HTI, various feedstocks have been examined for conversion to either fuels or chemicals utilizing both sub-bituminous and bituminous coal and heavy California (Hondo) oils. Each of the continuous bench scale test runs described herein used a proprietary dispersed iron catalyst called GelCat™.

Tables 1 and 2 present the comparison of runs using Black Thunder sub-bituminous coal, waste curbside plastics, and heavy Hondo resids co-processed in various combinations at several space velocities.

Table 3 shows further comparisons of liquefaction performance with coal and automotive shredder residue, with curbside plastics and plastics-derived pyrolysis oils.

HTI has accumulated extensive data on the direct liquefaction and hydrocracking of lignin, having tested this concept for various clients since the 1970s. Test results indicate that good conversion to phenol and cresol can be obtained using iron-based catalysts. The product oils from a Kraft lignin are a mixture of phenols and cresols as shown in Table 4. This wood waste is also a good source of fuels and chemicals when co-processed with coal and heavy-oil.

The world's vast resources of coal and heavy-oil can be utilized by processing to liquid fuels. The catalytic coal liquefaction process is technically well developed but not economical yet. An innovative process for addition of inexpensive hydrocarbons from MSW into the coal/waste liquefaction and heavy-oil/waste liquefaction processes should make these processes highly economic and, at the same time, alleviate the costly MSW disposal problem and help reduce carbon emissions through the use of renewables. A simplification of a process now under development at HTI is shown in Figure 2.

RESULTS AND CONCLUSIONS

Table 1 shows the operating parameters for the oil, plastics, coal combinations tested. As can be seen, feed conversions vary from 96 to 99.9 wt% maf. The addition of waste plastics shows an increase in residuum conversion and distillate yield. Waste curbside plastics as seen improve performance and also decrease hydrogen consumption due to the higher hydrogen content of the plastics versus the oil and coal feedstocks. Additionally, the addition of plastics controls the manufacture of undesirable light C₁-C₃ gas yields. Thus, the addition of plastics redirects hydrogen to the production of valuable liquids rather than gases.

As seen from Table 2, the overhead products are of excellent quality with high API to 50 and H/C atomic ratios close to 2.0 and nitrogen and sulfur contents below 15 ppm sulfur and 1 ppm nitrogen.

Table 3 represents a comparison of the performance of five run conditions, from the co-processing of auto shredder residue and pyrolysis oil. Co-processing of Black Thunder coal,

Hondo oil, and Auto Shredder Residue (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 production, but also reduces hydrogen consumption by about 2 W%. Economic analysis showed that by adding plastics to coal/ASR feedstock, the equivalent crude oil price dropped by \$6/barrel.

It was concluded that auto-fluff, containing primarily polyurethanes and high impact polystyrene as its principal polymeric constituents, was not as effective as the Municipal Solid Waste (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.

Pyrolysis oil derived from curbside plastics was co-processed with Hondo and Coal as seen in Table 3 with similar results as for the Coal/ASR (PB-04-4) with a slight decrease in hydrogen consumption. Run PB-06-4, a mixture of Hondo oil, pyrolysis oil, and coal, was operated at higher space velocity. Thus, resid conversion decreased; however, this was compensated for by a decrease in light gas yield and hydrogen consumption. The projected equivalent crude oil price for this was \$19.6/barrel.

The result and increase in the heating value of the clean solid fuel produced from MSW and the demonstrated conversion of lignin via hydrocracking justify examination of these feedstocks combined with coal, oil, and other waste feedstocks.

ECONOMICS

The examination and projection of plant costs associated with refinery companion plants (integrated) indicate that the co-liquefaction of waste with coal or oil provide a viable, secure alternative to the imported oil.

A techno-economic analysis for a site-specific waste/coal Direct Liquefaction plant at 10,000 bbls/day integrated into an existing refinery with random waste delivered to the plant shows an average required selling price at zero acquisition cost with a 15 percent ROI of \$16/barrel. With a portion of the tipping fees included, the price could be less than \$14/barrel and is cost-effective today. The current average US tipping fee is \$28/ton for land filling and \$54/ton for incineration. See Figure 3, which illustrates the change in product cost with tipping fee.

SUMMARY

Based on the encouraging results from these studies and the need to conserve materials and reduce emissions, continuing studies are warranted using readily available waste materials in combination with coal or heavy resids. The work can lead to the production of low-cost, clean transportation fuels and chemicals while protecting the environment.

FIGURE 1
HTI'S PILOT PLANT UNIT

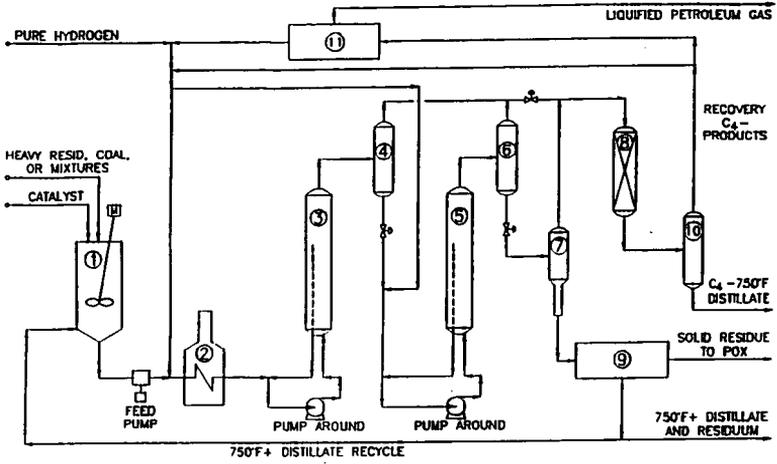


FIGURE 2
PROCESSING OF MUNICIPAL SOLID WASTE TO FUELS

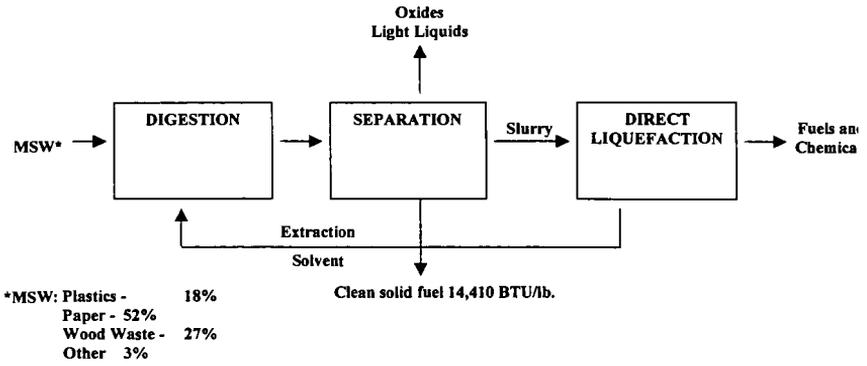


FIGURE 3
PROJECTED ECONOMICS OF CO-LIQUEFACTION
INTEGRATED WITH AN OIL REFINERY

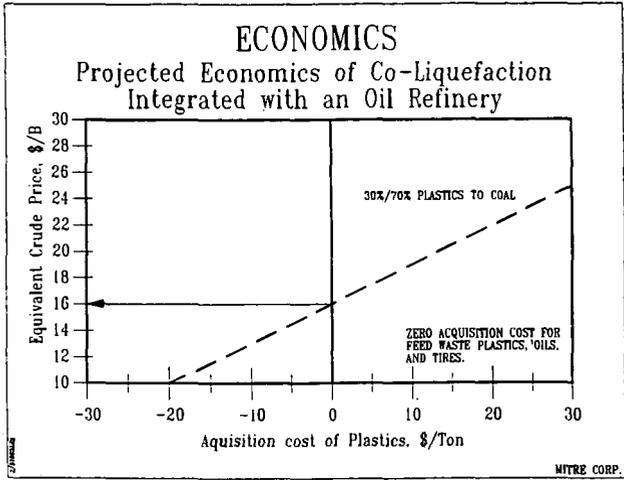


TABLE 1
PERFORMANCE COMPARISON - YIELDS

	OIL	COAL/OIL	COAL/OIL/ PLASTICS	OIL/ PLASTICS
Feed Composition, W%				
Coal, Black Thunder	0	50	33.3	0
Plastic, Curbside	0	0	33.3	50
Oil, Hondo Resid	100	50	33.3	50
Space Velocity, Kg/hr/m ³ rxn 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	51.1	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
PERFORMANCE OF COAL/WASTE CO-PROCESSING USING GELCAT™

Run ID	PB-04-03	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 GelCat™	1000	1000	1000	1000	1000
Mo	50	50	50	0	0
Space Velocity					
(kg/l/h 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

TABLE 4
300-465°F OIL COMPOSITION FROM KRAFT LIGNIN

	RUN 184-4	RUN 184-5
Phenol	6.5	7.8
o-Cresol	3.6	6.0
m-p-cresols	21.6	24.9
2,4 xyleneol	7.0	8.8
p-ethyl phenol	33.2	28.8
o-n-propyl phenol	8.0	9.1
p-n-propyl phenol	20.1	14.6
	100.0	100.0