

## STUDIES IN COAL/WASTE COPROCESSING AT HYDROCARBON RESEARCH, INC.

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**Keywords:** Waste Recycling, Catalytic Coprocessing, Co-Liquefaction

**ABSTRACT:** - The co-liquefaction of waste plastics with coal and waste tire rubber with coal was successfully demonstrated at a combined processing rate of 3 TPD at the Proof-of-Concept facility of Hydrocarbon Research, Inc. in Lawrenceville, N.J. The POC Program is jointly funded by the U.S. DOE, Hydrocarbon Research, Inc., and Kerr McGee Corporation. A total of 12 tons of plastics & coal and 5 tons of waste rubber tire & coal were processed to produce clean light distillates (IBP-343°C) with less than 40 ppm of nitrogen and 20 ppm of sulfur. Coal conversion was well maintained (92 W% maf) and nearly complete conversion of the organic waste to oils was achieved (65 W%+ maf distillate yields). Both the plastics and rubber contributed hydrogen to the liquefaction thereby reducing the hydrogen consumption by as much as 2 W% of the maf feed. This has a direct impact on reducing the cost of premium fuels from coal. Co-liquefaction of waste organic materials with coals provides for the recovery and recycle of waste materials back into the economy as premium fuels and feedstocks for petrochemicals. A concerted effort is underway to optimize the process to produce more value-added products with improved energy efficiency.

**INTRODUCTION:** - Increasing problems associated with waste disposal, combined with the recognition that some raw materials may exist in limited supply, dramatically increase interest in recycling. Recycling of paperboard, glass, and metal are well understood and these materials are now recycled in many areas around the world. Recycling of plastics presents greater technical challenges<sup>(1)</sup>, primarily due to the differences in the chemical compositions/properties of various types of plastics. Used automobile tires, the main source of waste rubber, pose another environmental challenge. Most of the 200 million used tires that are discarded in the United States every year, end up in stockpiles or landfills, although recently some use of scrap tires is also reported as fuel for power generation. Other reported methods of recycling the scrap tires are based on pyrolysis which results in low thermal efficiency and also poor selectivity to liquid fuels.

**RATIONALE:** - Coal is an abundantly available fossil fuel source with low hydrogen contents. The cost of hydrogen is a significant portion of the total cost of converting coal to refined transportation fuels such as gasoline, kerosene, and diesel via the state-of-the-art conversion technology. These municipal solid waste components such as plastics or hydrocarbon oil in used tires are relatively richer in hydrogen contents than coal. Thus, using these as a part of the feed in coal liquefaction would significantly reduce the cost of hydrogen production. There also seems to be a distinct advantage in processing plastics/rubber waste in a liquid phase or slurry mode under conditions much milder than those used in pyrolytic methods of conversion. Coal as a component of the feed mixture can thus provide not only a way to liquefy these waste stream, but can also act as a "mitigator" in maintaining the overall composition/properties of the combined feedstocks more uniform. This mediator role of coal is very crucial for any waste-stream conversion/recycling process because the waste streams, depending on location, are going to be inherently different in their compositions. Thus, it appears to be practical to co-process the most abundantly available fossil fuel, coal, with hydrogen-rich, though inhomogeneous in composition/properties, waste streams. Feed mixtures consisting of between 20-40 W% wastes (esp. plastics) are considered realistic and are being studied for catalytic slurry processing at Hydrocarbon Research, Inc. For used rubber tires, co-processing with coal can provide a better way for disposal while the carbon black component of the tires is reported to provide catalytic action during coal conversion reactions<sup>(2)</sup>.

**LABORATORY-SCALE WORK:** - Initial work carried out at Hydrocarbon Research, Inc., to a large extent, was a follow up of the research reported by the Consortium of Fossil Fuel Liquefaction Science<sup>9</sup>. It mainly constituted some microautoclave testing for the screening of the plastics feedstocks reactivity, process severity required, and the catalyst additive for plastics depolymerization. The lab-scale work focused primarily on the pure plastics, i.e., HDPE, Polystyrene, and PET, in the extrudate form. No lab-scale work was carried out in support of the coprocessing of used tire rubber with coal as HRI had a past experience in handling crumb rubber slurries from its H-Rubber process-related work. Our dissolution experiments with mixed plastics indicated that plastics (in coal/petroleum derived oil), especially HDPE, needed about 30-45 minutes at temperatures in excess of 220°C for complete dissolution. Adding coal to this plastics/oil mixture appeared to influence the fluidity of the total slurry in a positive way. The pre-mixed coal, plastics, and oil slurries at 33 and 50 W% of mixed plastics in solid feed exhibited a good pumpability behavior and when tested for reactivity in the 20 CC microautoclave at 440°C and 60 minutes reaction time, about 92 W% conversion to THF soluble products was obtained. Of the three plastics we tested individually at the lab-scale, HDPE was found hardest to convert while both the polystyrene and the PET converted almost completely under coal liquefaction condition.

**PDU-SCALE EXPLORATORY WORK:** - As a part of the US DOE sponsored Proof-of-Concept (POC) direct coal liquefaction program, the technical and operational feasibility of co-liquefaction of coal and plastics/rubber tire wastes was evaluated at a 3.0 TPD scale. A schematic of the HRI's PDU facility is shown in Figure 1. An eight day long extension of the PDU run POC-02 was carried out using Wyoming subbituminous coal from Black Thunder mine and pure forms of high density polyethylene, polystyrene, polyethylene terephthalate, and -20 mesh crumb tire rubber in a two-stage catalytic mode of operation, with an in-line hydrotreater. During the first six days, a total of 12 tons of mixed plastics were processed with coal (@30% plastics), while 5 tons of fiber-free -20 mesh crumb rubber tire (@26% of solid feed) was processed with coal during the last two days of continuous operation. The coal/waste feed was prepared in two steps: rubber/plastic waste was first slurried with recycle solvent and transferred to the slurry mix tank to which coal and more recycle solvent were added. It was found that a recycle solvent-to-solid feed ratio of about 2.25 was satisfactory for smooth pumping operations with plastics/rubber wastes. Some foaming problems were encountered at the slurry mix tank because of its high temperature and high moisture content of the feed coal. Table 1 contains detailed operating conditions. Because of the fact that the co-liquefaction operation/extension of the PDU run POC-02 was of short duration, the time allowed for process equilibration was not sufficient. As a result of this, the results obtained and presented in Table 2 should be considered with caution; also it should be viewed as directional data rather than an absolute performance during co-liquefaction. Table 2 compares the performance of the "coal-only" feed Period 36 with two coal-plastics cases (Periods 42 & 43) and one coal-rubber case (Period 45). The mixed plastic feed contained 50% HDPE, 35% PS, and 15% PET, simulating the compositions in a typical municipal solid waste. It can be seen from Table 2 that co-liquefaction resulted in a reduced hydrogen consumption, while maintaining total coal and resid conversions. The distillate liquid yields were also higher. The quality of the distillates obtained during the co-liquefaction periods was also premium with very low nitrogen and sulfur contents (Figure 2). Due to the overall process severity and short duration for the entire operation, a steady-state with respect to the recycle solvent was not achieved, i.e., significant portions of an external make-up oil had to be used to obtain a solvent/coal ratio of 2.25 (Figure 3). As a result, light fractions of the make-up oil were excessively hydrocracked increasing the yield of light gases. Some degradation of heavy co-liquefaction products was also noticed across the solids-separation Vacuum Tower/ROSE-SR systems.

**BENCH-SCALE WORK:** As a follow-up of the exploratory PDU scale test of co-liquefaction, a bench test is being conducted to delineate the effects of process severity, catalysis, feed composition during coal/plastics co-processing, when process is at steady-state and is under complete solvent-balance. The same mixture of co-mingled plastics, used earlier at the PDU scale, and Illinois No.6 Crown II mine coal is being evaluated in a 20 Kg/Day two-stage bench-scale unit. Preliminary results confirm our earlier findings at the PDU level. The process is being operated in a catalytic/thermal mode with sulfated iron-molybdenum dispersed catalyst only in stage II. For the first 14 days of this operation so far, solvent-balance conditions have been achieved. Preliminary results are about 6-8% gas yields, 71-73% distillate liquid yields, and 6-7% hydrogen

consumption (all on maf basis) result from co-liquefaction at the overall process severities lower than that at the PDU scale. The final results of this work will be conferred at the meeting.

**SUMMARY:** - Overall co-liquefaction operations at the PDU scale were successful and established both the technical and operational feasibility of the process. In general, high total (coal+plastics/rubber) conversions were obtained with high resid conversions; the yield of light distillates was high and distillates were of high quality (high H/C, very low N & S contents). We were also successful at establishing a procedure for preparation and pumping under high pressure of the feed materials that contain as much as 26 W% comingled plastics and/or crumb rubber. It is well understood that since insufficient time was allowed for the equilibration of the process, recycle solvent-balance was never achieved any time during the operations. The problem of solvent-balance maintenance during continuous operations is being currently addressed at bench-scale. Our ongoing work addresses all the above issues such as optimum process severity, catalysis, solvent balance, and process equilibration. The final results of our latest work in this area will be discussed during the final paper.

#### REFERENCES

- (1) "Recycling-Information pamphlet" from Dept. of Govt. Relations & Science Policy, Am. Chem. Soc., Washington, D.C.
- (2) Farcasiu, M., "Another use for old tires", ChemTech, Jan. 1993, pp. 22-24.
- (3) Proceedings of the Eighth Annual Meeting of the CFELS, Snowbird, Utah, July 1994.

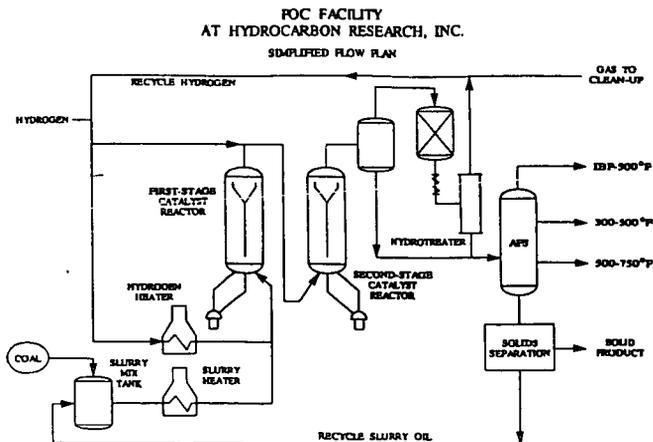


Figure 1

**Inspection of Naphtha Stabilizer Bottom  
SULFUR & NITROGEN REMOVAL**

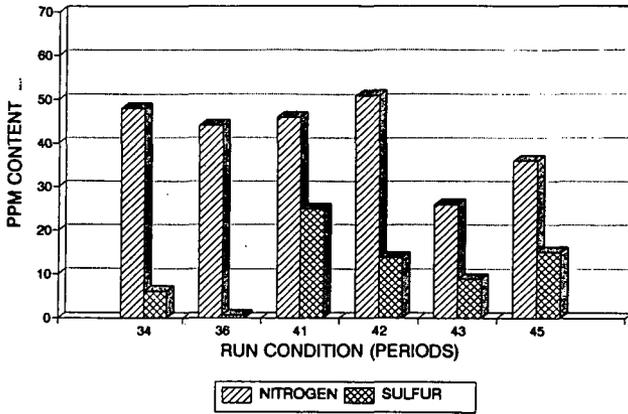


Figure 2

**POC-02 PDU RUN 260-005  
RECYCLE STREAM COMPOSITION**

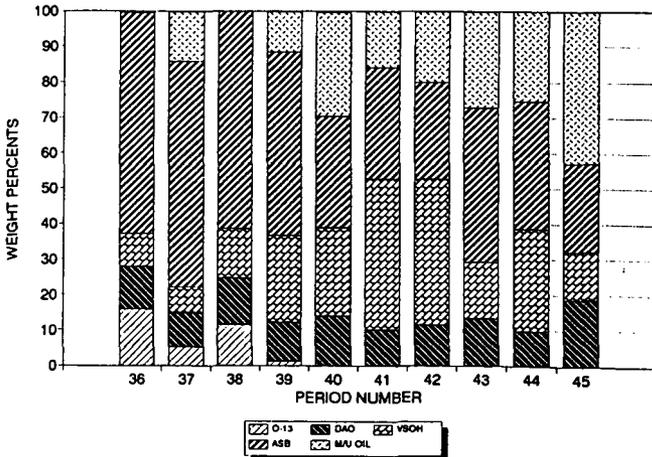


Figure 3

**Table 1. Operating Summary During Co-Liquefaction**

| Process Conditions                  | 5                | 6             | 6             | 7             |
|-------------------------------------|------------------|---------------|---------------|---------------|
| Period/s                            | Rose-SR<br>35-38 | Rose-SR<br>42 | Rose-SR<br>43 | Rose-SR<br>45 |
| Recycle Type                        | Ashy             | Solids-free   | Solids-free   | Solids-free   |
| Feed*, Wk%                          |                  |               |               |               |
| Coal                                | 100.00           | 88.00         | 70.00         | 74            |
| Plastics (42,43) & Rubber (45)      | 0.00             | 32.00         | 30.00         | 26            |
| HDPE                                | n/a              | 19            | 15            | n/a           |
| PS                                  | n/a              | 13            | 10            | n/a           |
| PET                                 | n/a              | 0             | 5             | n/a           |
| Ground Rubber                       | n/a              | n/a           | n/a           | 26            |
| Space Velocity, Kg/hr/m3            | 614.50           | 379.00        | 433.60        | 398.40        |
| K-1:                                |                  |               |               |               |
| Temperature, Deg. C                 | 432.20           | 428.30        | 431.10        | 430.00        |
| Cat Replac. Rate, Kg/Kg Ton MF Coal | 0.75             | 0.45          | 0.45          | 0.00          |
| Catalyst Age, Kg MF Coal/Kg Cat     | 1026.00          | 1044.00       | 1056.00       | 1072.00       |
| K-2:                                |                  |               |               |               |
| Temperature, Deg. C                 | 443.50           | 442.60        | 443.60        | 442.60        |
| Cat Replac. Rate, Kg/Kg Ton MF Coal | 1.25             | 0.90          | 0.80          | 0.00          |
| Catalyst Age, Kg MF Coal/Kg Cat     | 626.00           | 632.00        | 641.00        | 660.00        |
| <b>Flow Rates</b>                   |                  |               |               |               |
| Coal Feed, Kg/hr                    | 139.40           | 80.00         | 66.80         | 66.40         |
| Oil Streams to SMT                  | 0.00             | 29.24         | 29.50         | 23.30         |
| Plastics/Rubber                     |                  |               |               |               |
| O-43 Recycle to SMT, Kg/hr          | 67.85            | 103.50        | 64.66         | 71.56         |
| Make up Oil, Kg/hr                  | 0.00             | 40.00         | 58.53         | 93.52         |
| ASB (thru' COT) to SMT, Kg/hr       | 108.85           | 55.67         | 96.20         | 54.49         |
| Solvent/Coal Ratio, Kg/Kg           | 1.30             | 2.26          | 2.24          | 2.45          |

**Table 2. Process Performance During Co-Liquefaction**

| <b>Material &amp; Ash Balances</b>               |        |        |        |        |
|--|--------|--------|--------|--------|
| Liquefaction Section Recovery, Wk%               | 100.10 | 97.10  | 97.70  | 99.70  |
| Overall Material Recovery, Wk%                   | 99.35  | 97.80  | 100.30 | 98.80  |
| Normalization Factor                             | 1.00   | 1.03   | 1.02   | 1.00   |
| Ash Balance, Wk%                                 | 103.70 | 118.99 | 106.90 | 116.44 |
| <b>NORMALIZED YIELDS, Wk MAF FEED*</b>           |        |        |        |        |
| [Based on Liquefaction Section: O-13 Bottoms]    |        |        |        |        |
| H2S  | 0.56   | 1.61   | 1.25   | 2.25   |
| NH3  | 1.03   | 0.66   | 0.63   | 0.86   |
| H2O  | 19.28  | 14.72  | 18.56  | 16.30  |
| COx  | 1.16   | 0.49   | 0.99   | 0.83   |
| C1-C3  | 10.11  | 14.39  | 10.28  | 11.54  |
| C4-C6  | 4.50   | 7.77   | 4.17   | 6.61   |
| IBP-177 C  | 18.28  | 27.81  | 22.04  | 22.05  |
| 177-268 C  | 24.91  | 36.31  | 31.08  | 40.16  |
| 269-343 C  | 1.32   | 15.39  | 15.94  | 24.27  |
| 343-524 C  | 6.42   | -22.62 | -3.73  | -26.92 |
| 524 C+   | 12.01  | -0.42  | 0.10   | 3.79   |
| Unconverted Coal                                 | 8.51   | 7.20   | 7.20   | 5.32   |
| <b>PROCESS PERFORMANCE (Combined Feed Basis)</b> |        |        |        |        |
| Chemical H2-Consumption, Wk MAF                  | 8.05   | 8.34   | 6.50   | 7.47   |
| Total Feed Conversion, Wk MAF                    | 93.50  | 92.80  | 92.60  | 94.68  |
| 524 C+ Conversion, Wk MAF                        | 81.50  | 93.20  | 92.70  | 90.90  |
| Denitrogenation, Wk%                             | 68.25  | 77.40  | 78.00  | 74.60  |
| C4-343 C Net Distillates, Wk MAF                 | 49.00  | 90.30  | 73.20  | 93.10  |
| C4-524 C Distillates, Wk MAF                     | 57.50  | 67.70  | 69.50  | 66.20  |
| C1-C3 Selectivity, Kg/Kg of C4-524 C (x 100)     | 17.80  | 21.30  | 14.80  | 16.00  |
| H2 Efficiency, Kg C4-524 C/Kg H2                 | 7.16   | 10.70  | 10.70  | 8.90   |
| Deasher Coal Conversion, Wk MAF                  | 90.9   | 79.00  | 85.50  | 85.50  |

\*Fresh Feed\* is a combination of coal and plastics or coal and crumb rubber for Periods 42,43, & 45;