

COPROCESSING OF WASTE HYDROCARBON FEEDSTOCKS USING COUNTERFLOW REACTOR TECHNOLOGY

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INTRODUCTION

Like many jurisdictions in North America, the Province of Alberta is in the early stages of introducing measures to collect and recycle hydrocarbon wastes. In 1992 a levy of \$4 was added to the purchase price of each automotive tire. This levy was accumulated in a fund to promote the use and recycle of waste rubber tires.¹ The fund has supported several diverse uses of the waste tires, including incineration in cement kilns and rubber crumb generation for marketable products. To date these projects have only utilized 1.8 million of the 2.5 million tires which are discarded annually and have not started to reduce the backlog of over 4 million tires which was accumulated prior to 1992.

Recently several European plastics manufacturers have joined together to invest in a pilot project to convert waste plastic containers into oil.² In this process the produced naphtha will be converted into hydrocarbon monomers which can then be fed to polymerization units for complete recycle to fresh plastics. Similar efforts are underway in North America to recycle hydrocarbon wastes to oil or gaseous products. Much of this work is directed at co-liquefaction of polymers and coal, and has been reviewed by Huffman.³ Indications are that waste plastics and rubber tires can be converted into liquids using technologies which have been developed for the liquefaction of coal. Both Taghiei⁴ and Anderson⁵ have reported that there is a synergistic effect when coal and plastics are co-liquefied. Similarly enhanced coal liquefaction performance has been observed when co-liquefying waste tires and coal.^{6,7}

Alberta Research Council together with Canadian Energy Developments have developed technologies for the direct liquefaction of coal⁸ and coprocessing of coal and heavy oil/bitumen.⁹ It was a small step to envision the application of these technologies to the processing of other hydrocarbons such as waste plastics and rubber tires. This paper reports on a preliminary experimental program that was conducted to investigate the coprocessing of waste hydrocarbons with coal and heavy oil.

CO-LIQUEFACTION CONCEPT

The generic waste processing scheme is depicted in Figure 1. Initially there is a simple preparation step in which the waste hydrocarbon (and catalyst) is blended into a slurry with a recycle solvent or a refinery derived stream. Depending upon the feed characteristics the preparation step may be a digester to partially melt or solubilize the feed. The feed slurry is then introduced close to the top of the counterflow reactor (CFR) which is the heart of the process. This unit, operating at or near coal liquefaction temperatures and pressures, converts the hydrocarbon waste into liquid or gaseous products. The lighter boiling components are swept from the top of the reactors by the carrier gas. The carrier gas is most likely hydrogen but could be carbon monoxide or natural gas depending on the nature of the waste or solvent.

Light products are separated by conventional refinery processes. Liquid components from the bottoms slurry could be separated by a variety of procedures geared to the particular feed, including centrifugation, filtration or flashing. With plastic wastes the bottoms stream would be small and solids virtually absent. The withdrawal rate would then be dependant on the need for the slurry solvent. Tires produce a solid residue which if treated successfully could give regenerated carbon black and other byproducts.

EXPERIMENTAL

Alberta Research Council has traditionally employed 1 litre batch autoclaves as a screening tool to test new concepts or process operating conditions for the CFR. The procedures have been described elsewhere⁸. Feedstock properties are listed in Table 1. The solvent LO-6282 (boiling range 250-550°C) was obtained from the HRI facility

in Princeton, New Jersey. It was generated from a liquefaction run using Illinois #6 coal. Cold Lake heavy oil was taken from the Alberta Research Council Sample bank.

In a typical test, 75g of feed (polyethylene, coal, rubber crumbs or mixtures of each), was slurried with 150g of the solvent or heavy oil, and if required catalyst was added. The autoclave was charged to 1250 psi (cold) with hydrogen. This gave an operating pressure of 2000-2500psi depending on the process temperature or feed/solvent composition.

At the completion of the run the gas was discharged and the autoclave was flushed with hydrogen. The combined gas sample was analyzed by gas chromatography. The liquid slurry was recovered from the autoclave and a portion was subjected to extraction, either with tetrahydrofuran (THF) or sequentially with toluene, then THF.

Hydrocarbon conversion is reported as:

$$\frac{\text{Feedstock(DAF)}_{\text{In}} - \text{THF Insolubles}_{\text{Out}}}{\text{Feedstock(DAF)}_{\text{In}}} \times 100 \text{ weight\%}$$

where feedstock is polyethylene or rubber crumb or mixtures of either with coal.

In a limited number of runs a liquid sample was prepared by filtration to allow more detailed characterization.

RESULTS AND DISCUSSION

Co-Liquefaction of Polyethylene

The influence of temperature, catalyst and coal concentration, as well as a soak step were investigated for the co-liquefaction of polyethylene. By itself polyethylene proved intractable. At 425°C for 60 minutes, where coal conversion exceeded 90%, polyethylene conversion was barely 20% (Table 2). After correction for solvent decomposition, less than 1% of hydrocarbon gas was produced. Introduction of coal into the system improved feedstock conversion with Fe₂O₃ catalyst. Assuming that coal conversion at this temperature was 90% then the predicted feedstock conversion was calculated to be 28.3% with a coal to polyethylene ratio of 1:9, and 41.3% at a ratio of 1:1. Thus the experimental results suggest that there was a synergistic effect in this system. Product quality was visually poor; the almost clear polyethylene pellets had been transformed into a greyish rubbery solid. The hydrogen: carbon ratio of the solid residue from Run W-1 was 1.93, less than in the polyethylene 2.0. Further tests are in progress to determine if the polymer degradation products had incorporated chemically bonded solvent.

Increasing the process severity to 440°C for 30 minutes, and replacing the catalyst with the potentially more active molybdenum naphthenate (~600 ppm Mo on feed), improved feedstock conversion, but not to those levels which might be acceptable in a commercial process (nominally set at >90%). Polyethylene itself gave 65% conversion and almost the entire conversion product slate was a liquid (THF soluble). Coal addition did little to enhance the polyethylene conversion. Using an assumed value of 90% for coal conversion, the predicted values for feedstock conversion for Runs W-5 and W-6 matched the experimental.

The maximum potential for conversion and liquid yields had not been reached at 440°C/60minutes (Run W-7). Feedstock conversion had risen to 83% with the majority of the additional product being oils. Again assuming 90% coal conversion only 78% of the polyethylene had been solubilized or converted to gases. Therefore there was an opportunity to produce more liquid products from this feedstock combination by maximizing the process severity. This scenario was dependant on the stability of the solvent which at 440°C/60 minutes generated 2.3g of gas/100g solvent.

Finally the benefit of a soaking period prior to the hydroprocessing step was investigated (W-8). Polyethylene melts at ~125°C and a soaking or digestion step might help liquefy or solubilize the material and in a continuous operation improve flow and transfer characteristics of the feedstock slurry or solution. Dimethyl disulphide was also added to the charge as a sulphiding agent for the molybdenum. A small increase in feedstock conversion was recorded but it was

within the reproducibility of $\pm 2\%$ found in 1L batch autoclave tests. Hydrocarbon gas yield rose by about the amount attributable to the methane produced by the decomposition of the dimethyl disulphide.

Co-Liquefaction of Rubber Crumb

Following the preliminary program with polyethylene the conditions selected initially for rubber crumb were the relatively high severity $440^{\circ}\text{C}/60$ minutes using the molybdenum naphthenate catalyst. At these process conditions, Run W-9, the residual solids (THF insoluble), $34.7\text{g}/100\text{g}$ feed, corresponded almost exactly to the sum of the fixed carbon plus ash in the rubber crumb, $34.6\text{g}/100\text{g}$ (Table 3). Gas production was moderate at $3.9\text{g}/100\text{g}$ feed much of which can be attributed to decomposition of the solvent, i.e. $2.3\text{g}/100\text{g}$ solvent at similar process operating conditions. Product recovery and mass balances both for this Run and W-10, were well below the norm of 98-98%, which suggested that large quantities light hydrocarbons were produced and lost during the workup procedure. Characterization of the liquid product by simulated distillation indicated that the bulk of this material was within the naphtha boiling point range ($<183^{\circ}\text{C}$).

Introduction of coal into the feed, Run W-10, resulted in essentially complete conversion of both coal and rubber crumb. Using the previous value for rubber crumb conversion (Run W-9), the coal conversion was estimated to be greater than 95%. Gas production increased but was largely due to carbon oxides derived from the coal.

The above conditions were selected in most part to ensure coal liquefaction. Since the rubber crumb was at its maximum conversion, less severe condition might be effective. Lower temperature (375°C), in the absence of catalyst or hydrogen were taken as the opposite end of the spectrum of processing severity (Run W-13). Even so the liquefaction of the rubber crumb was then close to its maximum, 62.5% versus 65% for the high severity run. Gas production was minimal and product recovery was 99% indicating that fewer light hydrocarbon had been produced from the rubber or solvent. A simulated distillation of the filtered liquid product showed that the rubber crumb derived components were heavier than for the high severity run and were largely concentrated in the middle distillate fraction ($183\text{-}343^{\circ}\text{C}$).

Performance, in terms of rubber crumb conversion and production distribution, was unchanged when using the catalyst and hydrogen atmosphere at 375°C . Liquid product quantities increased due to the large uptake of hydrogen during the run (W-14). This contrasted with the nitrogen run where hydrogen was actually produced. Characterization of the liquid products by gas chromatography with a mass spectroscopy detector displayed a concentration of monocyclic hydrocarbons with isopropyl and methyl group attached to the ring. In the presence of hydrogen the cyclics were mostly cyclohexane or cyclohexene with lesser quantities of the corresponding aromatic analogues. In the nitrogen atmosphere the situation was reversed with the aromatics dominating. Still the presence of partially and fully hydrogenated rings pointed to the transfer of hydrogen from the solvent. This leads to the question of what type of solvent is the preferred medium. In coal liquefaction hydrogen donor and transfer properties are valued. With rubber crumb hydrogen donation may prove disadvantageous since the products formed by hydrogen addition may not be the best choice either for gasoline blending or as a petrochemical feedstock.

The proposed waste processing scheme would have to accept a variety of feedstocks and solvents. Alberta heavy oilsand bitumens are proven solvents for subbituminous coals.⁹ The effectiveness of Cold Lake heavy oil for solubilizing both coal and rubber crumb was demonstrated in Run W-12. Feedstock conversion was comparable with the LO-6282 solvent. The high severity led to low product recovery and very high hydrogen consumption. This was deceptive since consumption was reported on $\text{g}/100\text{g}$ feedstock basis (coal + rubber crumb) but much of the hydrogen would have been used during the upgrading of the bitumen. The same reasoning applies to gas yield which incorporates bitumen derived gases including hydrogen sulphide which had not been observed from the coal or rubber crumb.

CONCLUSIONS

Batch autoclave tests indicated that counterflow reactor technology was a promising procedure for co-liquefaction of waste plastics and rubber tires. The versatility of the process has been demonstrated by coprocessing coal, wastes and reactive solvent (heavy oil). It was successful at producing an all liquid slate of products from all the potentially convertible hydrocarbon in the rubber crumb.

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Figure 1
GENERIC WASTE PROCESSING SCHEME
USING COUNTERFLOW REACTOR TECHNOLOGY

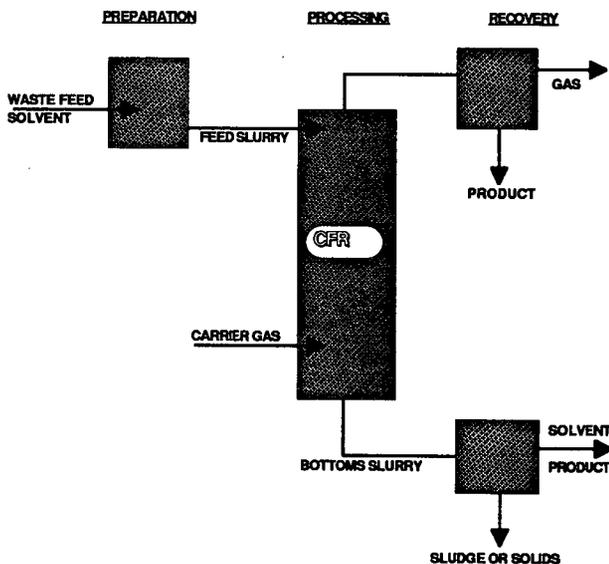


Table 1 Feedstock and Solvent Properties

	Rubber Crumb	Coal	Solvent LO-6282	Heavy Oil
Source	Alberta Environmental Rubber Products	Black Thunder	HF	Cold Lake
Nature	1 to 5mm	sub-bituminous	250-525°C	Full range
Characterization, Weight %				47% +525 resid
Carbon	83.1	71.0	88.5	82.8
Hydrogen	7.4	5.2	10.5	10.4
Sulphur	2.4	0.97	0.07	4.6
Ash	5.8	6.2		
Fixed Carbon	29.1	51.4	1.9*	12.6*

* Conradson Carbon Number

Table 2 Co-Liquefaction of Polyethylene

Run #	W-1	W-2	W-3	W-4	W-5	W-6	W-7	W-8
Feedstock								
PolyE	100	90	50	100	50	90	50	50
Coal		10	50		50	10	50	50
Catalyst		Fe2O3/DMDS			Mo naph		Mo naph	
Solvent		LO-6282			LO-6282		LO-6282	
Process Conditions								
Temperature, °C		425			440		440	
Pressure, psi(cold)		1250			1250		1250	
Time, min		60			30		60	
Process Performance								
Recovery, %	99	99	98	99	97	99	100	96
Conversion, weight %	19	35	61	64	72	62	82	84
Predicted@90%		28	43		75	66		
Yields, g/100gMAF feed								
Gas	3.2	4.1	7.3	2.0	6.8	2.9	8.8	9.4
Oils	16.9	33.0	36.2	63.2	66.2	59.6	74.1	77.1
Solids	81.1	64.6	38.9	35.7	27.9	38.2	18.4	15.7
Hydrogen consumption	1.21	1.67	2.39	0.89	0.98	0.66	2.32	2.14

Table 3 Co-Liquefaction of Rubber Crumb

Run #	W-9	W-10	W-13	W-14	W-12
Feedstock					
Rubber Crumb	100	50	100	100	50
Coal		50			50
Catalyst		Mo naph		None	
Solvent		LO-6282		Cold Lake	
Process Conditions					
Temperature, °C		440		375	440
Pressure, psi(cold)		1250		0(N2)	1250
Time, min		60		80	60
Process Performance					
Recovery, %		94		99	89
Conversion, weight %		65		62	64
Predicted@90%cc		77			77
Yields, g/100gMAF feed					
Gas		3.9		5.4	13.4
Oils		63.7		74.3	69.0
Solids		34.7		20.0	67.0
Hydrogen consumption		2.39		2.71	3.62
				-0.49	3.85
					8.71