

Cooperative Research Program in Coal-Waste Liquefaction

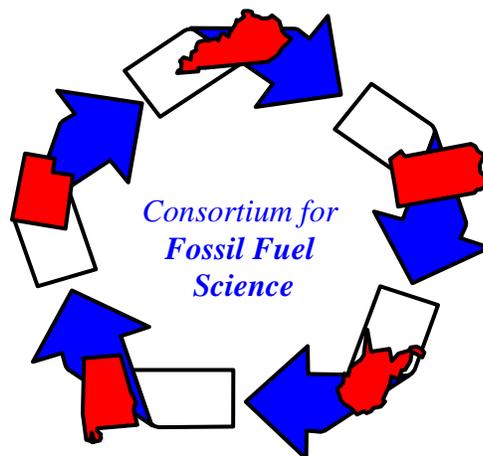
Final Technical Report
DOE Contract No. DE-FC22-93PC93053

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Feasibility Study for a Demonstration Plant for Liquefaction and Coprocessing of Waste Plastic and Tires

Final Technical Report for DOE Contract No. DE-FC22-93PC93053

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Abstract

The results of a feasibility study for a demonstration plant for the liquefaction of waste plastic and tires and the coprocessing of these waste polymers with coal are presented. The study was conducted by a committee that included nine representatives from the CFFS, six from the U.S. Department of Energy – Federal Energy Technology Center (FETC), and four from Burns and Roe, Inc. The study included:

1. An assessment of current recycling practices, particularly feedstock recycling in Germany.
2. A review of pertinent research, and a survey of feedstock availability for various types of waste polymers.
3. A conceptual design for a demonstration plant was developed and an economic analysis for various feedstock mixes.

The base case for feedstock scenarios was chosen to be 200 tons per day of waste plastic and 100 tons per day of waste tires. For this base case with oil priced at \$20 per barrel, the return on investment (ROI) was found to range from 9% to 20%, using tipping fees for waste plastic and tires typical of those existing in the U.S. The most profitable feedstock appeared to be waste plastic alone, with a plant processing 300 t/d of plastic yielding ROI's from 13 to 27 %, depending on the tipping fees for waste plastic. Feedstock recycling of tires was highly dependent on the price that could be obtained for recovered carbon. Addition of even relatively small amounts (20 t/d) of coal to waste plastic and/or coal feeds lowered the ROI's substantially. It should also be noted that increasing the size of the plant significantly improved all ROI's. For example, increasing plant size from 300 t/d to 1200 t/d approximately doubles the estimated ROI's for a waste plastic feedstock.

I. Executive Summary

Background: A feasibility study has been conducted for a demonstration plant for the liquefaction of waste plastic and tires and the coprocessing of coal with these waste polymers. A committee that included representatives from the Consortium for Fossil Fuel Science (CFFS), the U.S. Department of Energy (DOE) Federal Energy Technology Center (FETC), and Burns & Roe Services Corporation conducted the study. Members of the committee are listed in the table below.

CFFS	FETC	Burns & Roe
G.P. Huffman	M. Eastman	H. McIlvried
J. Zondlo	M. Baird	H. Schindler
L.L. Anderson	A. Cugini	J. Wilbur
I. Wender	S. Lee	R. Srivastava
M. El-Halwagi	U. Rao	
J. Tierney	K. Rothenberger	
N. Shah		
M. Shelley		
A.R. Tarrer		

Table 1. Members of the Feasibility Study Committee.

The principal results of the study are briefly summarized below.

Potential resource: Currently, approximately 50% of PET soft drink bottles and 30% of HDPE milk and water bottles are mechanically recycled (melted and re-extruded) in the U.S. Recycling of other types of waste plastic is very limited. Only about 5% of all waste plastic produced in the U.S. is currently recycled.

Similarly, the recycling of waste tires is very limited. Crumb rubber from waste tires is used to a limited extent as an additive for new tires, as an additive to asphalt, and for the production of mats used for playgrounds, running tracks and stables. Only about 15% of the used tires generated in this country are currently recycled. The use of tires as fuel (tire-derived fuel or TDF) is significant in some areas of the country but the committee does not consider that application to be recycling. It is estimated that approximately 75% of the used tires in this country end up in landfills, stockpiles or illegal dumps.

Approximately 30 million barrels of waste oils, greases, and fuels are generated each year in this country.

The total potential oil resource available from these petroleum-derived waste materials is estimated to be 148 million barrels per year. Additionally, there are several valuable byproducts that could be recovered. These include carbon black, steel wire, and aluminum foil. The total dollar value of this currently wasted resource is estimated to be over \$3 billion per year. Furthermore, if fossil resources such as coal and petroleum resid were coprocessed with these petroleum-derived wastes, the amount

of oil derived from this activity could be increased significantly.

German feedstock recycling industry: The country with the most aggressive recycling program in the world is undoubtedly Germany. The current report and two of its appendices contains a fairly complete discussion of the German waste plastic feedstock recycling industry. Members of the feasibility study committee received a great deal of information and assistance from representatives of the Duales System Deutschland (DSD) and their contractors, particularly at the waste plastics liquefaction plant at Bottrop, Germany, operated by Kohleöl-Anlage Bottrop, GmbH (KAB). Currently, DSD is supervising the recycling of approximately 300,000 tons of waste plastic per year. The operation includes collection, sorting, preparation of the material into a uniform feedstock, and processing into oil or other hydrocarbon products. The KAB liquefaction plant is currently converting 80,000 tons of waste plastic per year into high quality oil products. DSD also supports processing plants that convert the waste plastic into oil, olefins, synthesis gas, and reducing gases for production of steel in blast furnaces. Continuing interaction and collaboration with DSD and KAB will be valuable as an American industry in this area develops.

Research: The report summarizes the status of the research program on liquefaction and coprocessing of waste polymers sponsored by the DOE. Some of the results that are most pertinent for demonstration plant development are given below.

Plastic liquefaction and coprocessing: The liquefaction of commingled waste plastic typically yields 80-90% oil, 5-10% gas, and 5-10% solid residue. Oil yields and oil quality are improved by solid acid catalysts and metal-promoted solid acid catalysts. At temperatures above 440 °C, thermal and catalytic oil yields are comparable but lighter, higher-octane oil products with lower chlorine content are produced catalytically. No solvent is required but good results have been obtained with mixtures of waste oil and plastic. The reactions can be carried out at low hydrogen pressures (~100-200 psig) and with low hydrogen consumption (~1%).

Recent experiments by the CFFS have established that pyrolysis of waste plastic at 600-700 °C followed by hydroprocessing of the pyrolysis liquid is a good approach. Under optimum pyrolysis and hydroprocessing conditions, yields of high quality oil, low in chlorine, nitrogen and sulfur content, approaching 80% have been achieved.

Coprocessing of plastic and liquid products derived from plastic with both bituminous and subbituminous coal has been investigated. Generally, the best results are obtained using catalysts with both hydrogenation and hydrocracking functions, such as metal-promoted $\text{SiO}_2\text{-Al}_2\text{O}_3$ or mixtures of metal hydrogenation catalysts with HZSM-5. Oil yields of 60-70% and total conversions of 80-90% have been obtained. High hydrogen pressures (1500-2500 psig) and solvents with some aromatic character are required. Petroleum resid is found to be a good solvent for coprocessing of coal with plastic.

Rubber liquefaction and coprocessing: Crumb rubber is readily liquefied at 400 °C under low hydrogen pressures (~100-200 psig), yielding 50-60% oil, 5-10% gas, and 30-35% carbon black. The oil product is improved by the presence of a metal hydrogenation catalyst such as nanoscale iron or molybdenum sulfide. Experiments on the coprocessing of tire rubber with coal indicate that

rubber converts to oil in the same manner as it does when coal is not present. High hydrogen pressures and a hydrogenation catalyst are required for coprocessing of rubber and coal. The coprocessing of coal with pyrolysis oil derived from tires has been shown to be a viable approach.

Because of their relatively high content of inerts (25-30% carbon black, 10-15% steel wire and inorganics), the committee concluded that the best approach for tires is to pyrolyze them and hydrotreat the pyrolysis oil, either alone or in mixtures with hydrocarbon liquids derived from plastic or other sources. The carbon black and wire left behind in the pyrolysis process can then be readily separated as by products of the process. Experiments on the activation and upgrading of the carbon black are promising, yielding carbon products with surface areas of several hundred m²/g and ash contents of 1-2 %.

Although the experimental results show that coprocessing of plastic or rubber with coal is certainly feasible, it must be concluded that there is no major synergy resulting from coprocessing. Oil yields and total liquid yields determined from coprocessing experiments are generally close to the average of the yields obtained from the polymers and the coal separately. Moreover, the advantages of using lower hydrogen pressures and experiencing lower hydrogen consumption when liquefying plastic or rubber alone is lost when they are coprocessed with coal.

Plant design: A modular design was chosen for the demonstration plant. The three principal modules for the base design and their functions are described below.

1. Tire module - Tires are shredded to a nominal size of 2-4 inches and pyrolyzed at 600-700 °C. Pyrolysis oil from the tires is passed on to the upgrading module. Steel wire is magnetically separated from the pyrolysis residue to be sold as scrap steel, while the carbon black is activated by partial oxidation and then cleaned of remaining inorganic materials.
2. Waste plastic module – Two types of plastic module were considered. In the first, melting and partial depolymerization (M/D) of the plastic is carried out at a moderate temperature (~380 °C) over a long residence time (5-6 hours). Light, volatile oils are scrubbed to remove HCl, condensed, and passed on to the upgrading module. Aluminum foil and other inerts sink to the bottom of the M/D reactor and are removed. The aluminum is sold as a by-product. The heavy hydrocarbon liquid remaining in the reactor, which constitutes 60-70% of the plastic, is transferred first to a hydrocracking reactor, then to the upgrading module. This approach is similar to technology currently in use in Germany.

In the second type of waste plastic module, the plastic is subjected to pyrolysis at a higher temperature (~600 °C) for a much shorter residence time (~1 hour). Limestone or a sodium compound is added to the pyrolysis reactor to insure efficient capture of chlorine. The volatile product from this process is scrubbed and condensed, yielding about 10-15% gas and 75-80% of a relatively heavy oil product that is transferred first to a hydrocracking reactor, then to the upgrading module. This approach is based on research conducted by members of the CFFS. As discussed in detail in the report, the pyrolysis plastic module is projected to be more economical than the M/D plastic module and this is the preferred technology recommended by the feasibility study committee.

3. Upgrading module - Catalytic upgrading of the liquid products from modules 1 and 2 occurs in a slurry phase reactor using a dispersed, nanoscale, iron-based catalyst, followed by distillation of the upgraded product.

A modular approach was adopted to allow potential developers to choose the modules that best suit their needs. For example, if tire recycling is the main objective, modules 1 and 3 are needed. If converting plastics into oil is the primary interest, modules 2 and 3 are required. Several modular combinations are considered in the economic analysis.

Tires entering the pyrolysis reactor may be replaced by coal, while petroleum resid and waste oil may replace any of the liquids entering the upgrading module.

Economic analysis: The economic analysis was carried out for the modular plant described above for the following cases. (1) The *base case*: a plant liquefying 200 tons per day of waste plastics and 100 tons per day of tires (10,000 tires per day). (2) A plant liquefying 300 tons per day of plastics with no tires. (3) A plant liquefying 300 tons per day of tires (30,000 tires per day) with no plastics. (4) Replacement of 20% of the tires by coal. (5) Replacement of 20% of the liquid entering the upgrading module by petroleum resid or waste oil. (6) The effect on the economics of increasing the size of the base case plant.

The uncertainty in the results of the economic analysis is fairly large ($\pm 30\%$) because: (1) the small size of the plant (300 tons/day) necessitated scaling down costs from much larger units; (2) equipment costs quoted by different vendors varied significantly; and (3) the committee identified several areas related to plant design that require further research.

Despite these uncertainties, the results of the economic analysis should provide useful guidelines to potential developers of a demonstration plant. A summary of the results for various plant development scenarios is presented in the table below. The estimated capital cost is given for each type of plant considered and the range of returns on investment (ROI) is given as a function of tipping fees and oil price. A major factor determining the range of the ROIs is the size of the tipping fees received by the plant for waste plastic and tires. In the table, results are presented for plastic tipping fees of \$30 and \$60 per ton, which is typical of current landfill tipping fees in various parts of the U.S. A wider range is considered in the report. For tires, a tipping fee of -\$20 per ton indicates that the developer has elected not to shred tires at the plant, but to buy shredded tires from a waste tire processing company at a cost of \$20 per ton. A tipping fee of \$75 per ton (\$0.75 per tire) is what the developer could reasonably expect to receive if whole tires are delivered to and shredded at the plant. The economics are clearly improved by shredding tires at the plant, particularly for a plant that processes only tires. It is also seen that increasing the value of the carbon derived from the tires has a significant economic impact.

These results are encouraging. For the base case (200 tons per day of waste plastic, 100 tons per day of tires), the predicted ROI with oil priced at \$20 per barrel is 9-20%. For a plant processing plastic alone, ROIs up to 21% are predicted, while a plant processing tires alone could achieve a ROI up to 34%. With an increase in the price of oil to \$25 per barrel, ROIs for these cases up to 25-38% are

expected. However, replacement of 20% of the tire feed by coal or 20% of the liquid by waste oil/resid causes decreases of several percent in the ROI.

Table 2. Summary of estimated capital costs and ROIs for various plant scenarios.

		Tipping fees /prices - \$/ton or barrel				
		Plastic tipping fee ←	30	30	60	60
		Tire tipping fee (+) or price (-) ←	-20	75	75	75
		Oil price ←	20	20	20	25
Type of plant	Capital cost (\$ million)	ROI (%)	ROI (%)	ROI (%)	ROI (%)	
Base case: 200 t/d of plastic, 100 t/d of tires	41.1	8.7	15.6	20.4	25.4	
Base case with 20% of tires replaced by coal	41.1	7.7	13.0	17.8	---	
Base case with 20% of liquid replaced by waste oil or resid	41.1	7.4	11.1	13.0	---	
300 t/d of plastic	39.8	13.0	13.0	20.5	26.7	
300 t/d of tires - carbon @ \$200/t	28.0	4.1	34.1	34.1	38.5	
300 t/d of tires - carbon @ \$500/t	28.0	22.5	51.9	51.9	56.3	
Base case - 600 t/d (400-plastic, 200-tires)	66.8	---	23.4	29.3	---	
Base case - 1200 t/d (800-plastic, 400-tires)	108.6	---	33.0	40.3	---	

Also included in the table are the results for several cases that achieve significantly higher ROIs. For example, if a higher price were obtained for the carbon derived from tires (\$500/ton or \$0.25/lb.), a plant processing 300 tons of tires per day (no plastic) could achieve a ROI of over 50%. It is also well known that larger plants are more economical. It is seen that a 600 ton/day plant could achieve ROI levels of 23-29%, while a 1200 ton per day plant could yield a ROI in the 33-40% range at current oil prices and tipping fees.

Future Program: The results of the current feasibility study indicate that a new industry can be developed to convert waste polymers and fossil energy resources into high quality oil and valuable by-products. *It is considered significant that the economic analysis predicts, for the first time, that a direct liquefaction process can be profitable and return a reasonable ROI at current oil prices, even at the demonstration plant stage.*

As noted earlier in this report, the resources currently wasted by disposal of plastics and tires in landfills includes approximately 120 million barrels of oil and hundreds of thousands of tons of carbon, steel and aluminum. However, plastics and tires constitute only about 12-14% by weight of all the waste materials that are landfilled. Other materials, such as paper wastes, yard wastes, wood wastes, biomass, and automobile shredder residue, are also largely hydrocarbon-based and constitute a larger percentage (50-60%) of landfill mass. It therefore seems logical to investigate the conversion of these materials into valuable hydrocarbon fuels or chemicals in future research.

Ideally, it would be advantageous to incorporate the conversion of these waste materials with the conversion of coal, possibly within the setting of an integrated gasification combined-cycle (IGCC) power plant. Pyrolysis, gasification, syngas reaction, activation, upgrading and hydroprocessing would be integrated to achieve the most efficient conversion of different types of waste materials into valuable hydrocarbon products. The Feasibility Study Committee strongly recommends that the U.S. Department of Energy support such a program.

II. Introduction

Mission:

During the past several years, the U.S. Department of Energy has sponsored a research program on the conversion of waste polymers into oil and the coprocessing of coal and waste polymers into oil using direct liquefaction technology. The research has been carried out by a combination of academic, industrial and government scientists and engineers. The principal academic participants have been the members of the Consortium for Fossil Fuel Science (CFFS), a five university research consortium with participants from the University of Kentucky, Auburn University, the University of Pittsburgh, the University of Utah and West Virginia University. Most of the laboratory scale research has been carried out by the CFFS. Hydrocarbon Technologies, Inc. (HTI), where pilot scale and continuous tests have been conducted, Consol, where specialized analytical techniques have been employed, and the Mitre Corporation, where economic analyses have been carried out, have provided industrial participation. The in-house research staff at the Federal Energy Technology Center (FETC), Pittsburgh, has conducted a variety of experiments to complement work in the academic and industrial sectors.

Based on very successful laboratory and pilot scale experiments and promising economic analyses, DOE/FETC commissioned the CFFS to conduct a feasibility study for a first demonstration plant for this technology. To carry out this study, a committee was established that included participants from the CFFS, FETC and Burns & Roe Services Corporation. The feasibility committee membership is given on the title page of the report. The goals of the study were as follows:

1. To establish a conceptual design for a demonstration plant for direct conversion of waste polymers and coal into oil products.
2. To carry out an economic analysis and environmental assessment for the demonstration plant.
3. To develop a group of stakeholders from industry, state and local governments and elsewhere with an interest in commercial development of the technology.

Potential Resource and Current Practice:

Currently, over 44 billion lbs. of waste plastic ⁽¹⁾ are disposed of in the U.S. each year. This is approximately 175 lbs. of waste plastic for every man, woman and child in the country. Although practice varies greatly in different parts of the country, only about 5% of all waste plastic are now being recycled. For plastic, recycling in the U.S. is primarily mechanical recycling; that is, melting and re-extruding used plastic into recycled plastic components. Uncolored high density polyethylene (HDPE), or milk jugs, is the preferred feedstock for this type of recycling, although colored HDPE can also be used for some types of products, such as plastic lumber, park benches, and marine pilings. Polyethylene terephthalate (PET), used primarily for soft drink bottles, can be recycled into synthetic fibers and carpet feedstock. With the exception of milk jugs and soft drink bottles, however, only a very small percentage of waste plastic is recycled. According to the EPA, ⁽²⁾ approximately 50% of PET soft drink bottles and 30% of HDPE milk and water bottles are recycled but only about 5% of all waste plastic is recycled.

Over 280 million automotive tires ⁽³⁾ are disposed of annually in the U.S., or approximately one tire (~20 lbs.) for each person. Furthermore, it is estimated that there are 4 billion tires “on the ground”

in this country. Tires are combusted, usually with coal, in utility boilers to produce electricity⁽⁴⁾ and they are burned in cement kilns. Although these methods of utilizing waste tires are productive, they are not recycling. As part of this study, two trips were made to Rochez Bros., Inc., a tire recycling business located in the Pittsburgh area. The information obtained during these trips and from other sources has been summarized in a report by Zondlo⁽⁵⁾ that is included as Appendix A to this report. Normally, the tires are shredded to a nominal size of 2-4 inches prior to sale to utilities for combustion. Most companies in the tire recycling business receive a tipping fee of \$0.75 - \$1.00 per tire and it is estimated that they approximately break even at the point where the tires are shredded to this size and loaded in trucks for shipment to utility companies. The price paid by utilities for shredded tires is approximately \$20 -25 per ton. At a shred size of 2-4 inches, most of the steel wire is retained in the tires but this does not appear to have a major effect on furnace operation. The steel is apparently readily incorporated into the slag or ash.

A smaller percentage of used tires are shredded to small particle sizes, either by means of recycling through the shredder with finer screen sizes or using such methods as cryogenic comminution, which produces a product known as crumb rubber.⁽⁵⁾ Steel wire is separated in the process by magnetic and other methods and can be sold as scrap steel. Depending on the final particle size of the rubber product, it can have a number of uses. These include use as additives for asphalt⁽⁶⁾ and fabrication of rubber mats for a variety of uses, including playgrounds, running tracks and stables. Crumb rubber can also be combined with plastics and used to form extruded solid components for a variety of applications. Finally, a small percentage of crumb rubber (5-10%) from used tires can be added back into new tires; this may be required for new cars by automobile manufacturers in the near future. The cost of producing crumb rubber is approximately 10-20¢ per pound and it is normally sold for 40-50¢ per pound.⁽⁵⁾ Approximately 15 % of the used tires disposed of each year in this country are recycled, according to the latest EPA report.⁽²⁾

Waste oils, greases and fuels are also considered in the current report. Although they are not solid polymers, they are also petroleum derived and coprocess with waste plastics and rubber extremely well, yielding a clean, upgraded oil product. Currently, approximately 30 million barrels of waste lubricating oil, grease and fuel must be either reprocessed or disposed of in the U.S. each year.⁽⁷⁾

The quantities of oil and valuable by-products that could be recovered by liquefaction and upgrading the waste polymers generated annually in the U.S. are readily estimated, as summarized in Table 1. Here, a yield of approximately 5 barrels of oil per ton of hydrocarbon feedstock is assumed. For waste plastics, the result is 110 million barrels. For tires, liquefaction could yield up to 8 million barrels of oil. Important byproducts include approximately 840,000 tons of carbon black and 280,000 tons of steel wire from the tires, and 440,000 tons of aluminum foil from the plastics. The aluminum foil is derived from aluminized Mylar labels and from lids used with plastic containers; a conservative estimate of the amount of aluminum foil in waste plastic is 0.5 %.

Table 1. Summary of potential products from waste polymers generated annually in the U.S.

Waste polymer	Tons/year	Oil yield (barrels/yr)	By-product (tons/yr)	Value (\$/yr)
Plastics	22 million	110 million	Al foil (110,000)	22,000,000
Tires	2.8 million	8.4 million	Carbon black (840,000)	168,000,000
			Steel wire (280,000)	14,000,000
Waste oil		30 million		
Total Oil		148 million		2,960,000,000

Total Potential Product Value - \$3,164,000,000

In arriving at the dollar values of the potential products in Table 1, rather conservative values have been assumed, as follows:

scrap aluminum \$200/ton
scrap steel \$50/ton
carbon black \$200/ton
oil \$20/barrel

In addition to the loss of this potential revenue, approximately a billion dollars per year is currently being paid in tipping fees to put most of these waste materials into landfills.

Finally, the potential oil resource could be increased significantly (possibly doubled) by coprocessing of these wastes with coal and petroleum resid.

III. Current practice in Germany

The country with the most aggressive recycling program in the world is undoubtedly Germany. The German recycling industry has developed in response to very restrictive legislation, particularly in regard to packaging. In simple terms, the law says that 80% of all consumer packaging materials must be recovered and 80% of all materials recovered must be recycled. The burden for achieving this goal is put on the manufacturer and the retailer. It should be emphasized that the law does *not* consider combustion of waste packaging to produce electricity to be recycling. Recycling is defined to be either mechanical recycling or feedstock recycling. The latter term includes conversion of plastics into oil, chemical feedstocks or useful hydrocarbon gases such as synthesis gas or reducing gases for steel production.

The response of German industry to this law has been the creation of the Duales System Deutschland or DSD. Member companies of the DSD place a surcharge (roughly a penny) on every container they sell. Each container that is subject to the charge is labeled with a small green, circular recycling symbol, the “green point” (der grunepunkt). The money collected is used by the DSD to support the recycling industry required to comply with the law. Currently, about \$4 billion DM (\$2.7 billion) is collected each year. This money is used to subsidize companies that collect, separate, prepare and recycle waste packaging material. For plastics, the term recycle includes both conventional mechanical recycling and feedstock recycling.

As part of this feasibility study, two trips were made to Germany and elsewhere in Europe by feasibility committee members and several trips to the U.S. have been made by representatives of the German recycling industry. Visits to tour the German waste plastics sorting, preparation and processing plants were made by Dr. Gerald Huffman, Dr. Naresh Shah, and Dr. Larry Anderson. The information gathered in these visits is summarized in two trip reports that are included as Appendices B and C to this report.^(8,9) Visits to the U.S. were made by Dr. Gerhard Fahrback of DSD to meet with the feasibility committee and to visit several of the CFFS universities and FETC; by Dr. Rolf Holighaus to participate in the annual CFFS Technical Meeting; and by Dr. Holighaus and Mr. Fritz Wenzel of Kohleöl-Anlage Bottrop (KAB), a division of Veba Oil, and to visit several of the CFFS universities for discussion of technical problems of mutual interest. These contacts have been quite valuable and informative.

A critical component of the German program is the separation of wastes that occurs at the household level. This has been achieved through a massive educational and advertising program sponsored by DSD. An important aspect of this program is educating school children about the importance of recycling. The garbage is separated into three principal components: containers and packaging material; paper products; and everything else. For reasons that are not clear, the packaging material includes both plastic and metal containers; it would seem preferable to separate these two types of packaging. Newspapers and glass containers are separated and delivered to collection centers by consumers.

All packaging materials, which include most of the plastics in the municipal waste stream, are collected in yellow plastic bags. The yellow bags are then delivered to sorting plants where the packaging materials are broken down into several components by a variety of mechanical, magnetic and manual separation methods. These components include aluminum and steel cans, rigid plastic bottles and other containers, large plastic film material (plastic bags) and everything else. The “everything else” is what is usually referred to as commingled waste plastics (CWP).

Sorting plants: Separation of the waste packaging materials occurs in sorting plants (Appendix C). As part of this study, a visit was made to a sorting plant in Worms, Germany, that separates about 7,000 tons of mixed waste plastic per year. The separation is accomplished both manually and by a variety of automated devices. The yellow bags are first opened and their contents distributed onto conveyor belts. All the material is conveyed into a large tumbling screen to separate material smaller and larger than ~200 mm in size. Most of the cans are separated into the smaller size stream.

The two separated streams are then sorted mechanically and magnetically. Air and screen separation is used to separate paper, plastic films and plastic bottles, while magnetic and eddy current separation devices are used to separate steel and aluminum cans. Aluminum cans with steel tops are a problem in these separation systems. The material sorted positively (bottles, large plastic films, and cans) is removed into appropriate bins. All remaining material is then passed on to a conveyor belt between two lines of 9-10 workers on each side who manually remove and toss into bins different items from the stream that can be mechanically recycled. What is left at the end of the line (about 60-70 % of the incoming material) is mainly mixed waste plastic. It is compressed into bales that are bound by steel wire and then transported by truck to the shredding/agglomeration (S/A) preparation plants. The positively sorted plastic can be mechanically recycled. It has a higher value than the mixed waste plastic and the sorting plant has the liberty to either utilize or sell it. At the plant in Worms, they were mechanically recycling most of the positively sorted material themselves, producing new yellow collection bags, plastic lumber, plastic benches, and plastic highway abutments.

The overall impression from this plant visit was that DSD is paying heavily for manual sorting in order to meet quota requirements for the percentage of waste plastics that are recycled mechanically. The magnetic, eddy current, air separation and screening steps are quite effective in removing metal cans and separating a great deal of the mechanically recyclable plastics (principally bottles and large films). Incorporation of these methods at U.S. recycling centers would be very worthwhile. However, attempts to legislatively set quotas for minimum percentages of waste plastics that must be mechanically recycled should be resisted in order that expensive manual labor can be avoided as much as possible. The approximate breakdown of waste plastics collected and separated annually into different fractions by the separation plants funded by DSD is shown in Table 2.

Fraction	Quantity (tons)	% of Total
EPS	3,500	0.6
Cups	10,000	1.9
Bottles	53,000	9.8
Film	143,500	26.6
Mixed Plastics	330,000	61.1
Total	540,000	100

Table 2. Summary of quantities of waste plastic fractions collected by the DSD in 1995.

Preparation plants:

The mixed waste plastic bales are then transported by truck to preparation plants. As part of this study, several German preparation plants were visited. Each of these plants processes from 10,000 to 60,000 tons of waste plastics per year. Currently, there are 10 preparation plants in Germany and one new plant is under construction. These preparation plants are currently capable of processing approximately 300,000 tons of waste plastics per year.

On arrival at the preparation plants, the bales are inspected visually and from one to several bales are opened and manually sorted to make sure that they contain primarily mixed plastic waste with very

little impurity contamination (metals, glass, paper, etc.). If this inspection is not satisfactory, the whole truckload is sent back to the sorting plant. The bales are then fed to a shredder where the waste plastics are reduced in size to pieces ranging from several mm to several cm. The stream is then passed under a magnetic separator to remove iron contaminants and other magnetic materials and is passed through an air-drying and separation system, where heavy impurities, such as glass and stones, and light impurities, such as paper, are removed. ***The DSD program has established that dry preparation is always cheaper than wet preparation.*** The material goes onto a vibrating screening table, where more separation of small (<5 mm), heavy components (glass, stone, etc.) occurs and oversize material (>100 mm) is directed back through the shredder. The shredded waste plastic is then subjected to further magnetic separation to remove remaining iron and magnetic tape impurities and is passed through an eddy current magnetic separation unit to remove aluminum foil. The shredded (<100 mm), cleaned, mixed plastic is then fed into a temporary in-line storage silo before sending it to a system of agglomerators.

Four agglomerators process the shredded plastic from each shredding and cleaning line. Each agglomerator has its own hopper, which is filled by a scrapper chain conveyor line with approximately 50-75 kg of shredded, cleaned, mixed plastic. A pneumatic valve introduces this plastic into the agglomerators, which are the same diameter as the hoppers. In the agglomerator, the shredded plastic is ground and compressed by a rotating grinding apparatus somewhat similar to a coffee mill. This homogenizes and partially melts the plastic from heat due to friction. A 350 kW motor runs a rotating blade continuously at 1500 rpm in the agglomerator. Water is sprayed on the hot (110-130 °C) plastic simultaneously, generating steam and embrittling the plastic, making it easy for the rotating blade to cut it into small granules. The steam generated is condensed and filtered. A gate near the bottom is opened to discharge the granules onto a vibration conveyor. The entire fill-grind-spray-chop-discharge cycle is about 4 minutes long. Gases and dust from the agglomerators are carried with the steam into canopy hoods near the discharge and taken to the gas clean up system.

The granulated material leaving the agglomerators is conveyed by belt to a "nosehole" screening system to remove oversize material (leather, fabric, and some PET, which has too high a melting temperature to be readily incorporated in the granules). Some aluminum is liberated during agglomeration and is removed by eddy current separation. The product is finally sieved for size. Material within size specifications (~1-10 mm) is conveyed onto the trucks. Fines contain predominantly paper and PVC, which is more brittle than the other plastics. The fines typically contain 7-8% Cl and are landfilled. Oversize material is sent through a small re-chipper, re-screened, and eventually sent to the trucks. Schematic diagrams and more detailed descriptions of a preparation plant are available in Appendix C.

Trucks transport the product to an adjacent warehouse. For every truckload, the ash, moisture and chlorine content and the density are measured. Specifications that the processed plastics must meet are summarized in Table 3. In order to meet these specifications, piles from various shredding and agglomeration runs are blended together as necessary before they are loaded into the larger

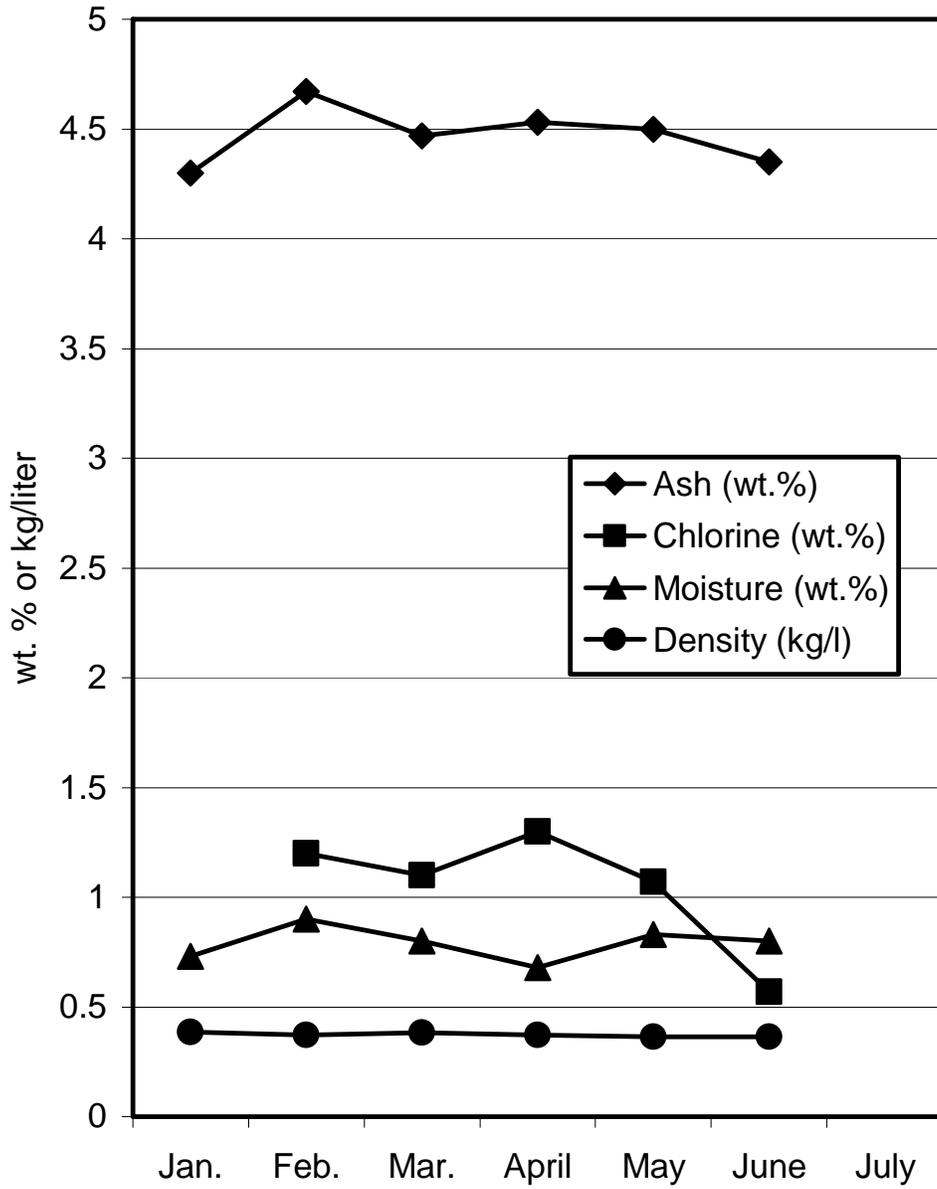


Figure 1. Monthly average of ash, chlorine, moisture and density for granulated waste plastic from a DSD preparation plant.

trucks that convey the granulated waste plastic to the processing plants. Figure 1 shows the monthly average of ash, moisture, chlorine and density over a six month period for their largest preparation plant. Currently, DSD operates 10 preparation plants with an output of 289,000 tons per year.

Property	Specification
Granular size	≤1.0 cm
Granular fines (<250 μm)	≤1.0 wt.%
Appearance	Pourable
Moisture content	<1.0 wt.%
Density	≥0.3 kg/l
Chlorine	≤2.0 wt.%
Ash (@650 °C) Total	≤4.5 wt.%
Ash (@650 °C) Metal	≤1.0 wt.%
Plastic content – Total	≥90.0 wt.%
Plastic content – Polyolefin	≥70.0 wt.%
Plastic content – Engineering resins	≤4.0 wt.%

Table 3. DSD product specifications for granular waste plastic agglomerate used for feedstock recycling.

Processing plants: The DSD supports several processing plants that carry out various types of feedstock recycling of plastics. The feedstock for all of these plants is the granulated waste plastic agglomerate described above. The availability of a relatively uniform granular feedstock is important for maintaining smooth operation of the processing plants. The processes used in the largest of these plants are briefly summarized below.

Liquefaction: This is carried out at Bottrop by Kohleöl-Anlage Bottrop, GmbH (KAB) at a plant that was formerly operated as a coal liquefaction pilot plant. The plant is currently processing approximately 80,000 tons of the DSD waste plastic agglomerates per year. Of the existing processing plants in Germany, this plant is closest to the conceptual designs discussed in this feasibility report. A rather complete discussion of the plant is given in one of the trip reports mentioned earlier (Appendix B ⁽⁸⁾) and in a forthcoming publication ⁽¹⁰⁾ and will not be repeated here. Briefly, the plant consists of a melting/depolymerization (M/D) unit, a thermal hydroprocessing reactor and a catalytic hydroprocessing reactor. A relatively low temperature (380 °C) and long residence time (5-7 hours) are used in the M/D reactor. In the M/D reactor, part of the plastic is volatilized. A low viscosity liquid is condensed from the volatile component and HCl is removed by scrubbing. The HCl is recovered as a byproduct; approximately 80% of the chlorine in the plastic feedstock is removed in this step. The plastic remaining in the M/D reactor is converted to a heavier, higher molecular weight, liquid. At 380 °C, this liquid has a relatively low viscosity and Al foil and other inerts sink to the bottom of the reactor. There the Al foil is removed and recovered as a byproduct by a patented KAB technique that utilizes reverse washing with a small amount of fuel oil.

The liquid from the M/D reactor is fed to a noncatalytic liquid phase hydrogenation reactor where thermal hydrocracking occurs. The reactor temperature is about 420 °C and the hydrogen pressure is approximately 50 bar (725 psi). CaO is added at four times the required stoichiometric amount to remove the remaining Cl as CaCl₂. The product, which is mainly volatile, passes through a hot separator and vacuum distillation to separate products from inerts and unconverted hydrocarbons. The volatile products pass to a gas phase hydrogenation reactor that uses a conventional NiMo/Al₂O₃ hydrogenation catalyst to hydrogenate unsaturated hydrocarbons, remove heteroatoms and hydrocrack some heavy molecules. Gas products and the synthetic crude oil product are then separated in a cold separator.

BASF Process: BASF has developed a multistage pyrolysis/distillation/gasification process for recycling waste plastic. In the first stage, the DSD plastic agglomerates are melted and heated to 300 °C where dehydrochlorination of PVC takes place. In the second stage, the melted plastics are heated to above 400 °C, causing thermal cracking of the polymers to yield various oils and gases. In the third stage, the oils are distilled to recover naphtha, long chain olefins, aromatic compounds and heavy oils. These products are processed in existing plants at the BASF Ludwigshafen works. Naphtha is fed to a steamcracker to recover monomers such as ethylene and propylene, the aromatic fraction is processed in an aromatic plant, and the heavy oil is converted into syngas in a gasification plant. No hydrogen is added and all processes are run at low pressures. A more complete description is available in Appendix B. The BASF plant, which was processing 15,000 tons of waste plastics per year at the BASF Ludwigshafen works, has recently ceased operations.⁽¹¹⁾ The reason given was that BASF wanted to increase the size of the plant to 300,000 tons per year to improve economics and the DSD could not guarantee them sufficient feedstock at the required tipping fee.

Gasification: The largest gasification plant in the DSD system is that of the “Sekundarrohstoffverwertungszentrum” (SVZ) in Schwarze Pumpe, where about 60,000 tons per year of waste plastics are gasified. It is a fixed bed gasifier of the Lurgi type. The DSD waste plastic granules are pressed into briquettes and gasified together with lignite and sewerage sludge. The mix is about 30-40 % plastic and 60-70% lignite + sewerage sludge. The briquettes are reacted with oxygen and steam at 800 °C to produce syngas (principally CO and H₂). The synthesis gas is used as the feedstock for further processes, such as methanol synthesis. In the gasification process, volatile tars are formed. These must be condensed, then fed to a second entrained flow gasifier. The tar contains 5-10% ash and is very heavy and difficult to feed. More serious feeding problems are encountered when attempts are made to feed the waste plastic granules from the preparation plants directly to the entrained flow gasifier. They melt and plug up the system. They are considering using the KAB melting/depolymerization (M/D) process and feeding the liquid product into the entrained flow gasifier.

Rheinbraun AG operates a smaller (12,000 tons per year) waste plastics gasification plant. It is a high temperature Winkler gasifier in which the waste plastics are gasified in a fluidized bed of air and steam at temperatures up to 950 °C. Synthesis gas is again the product.

Blast furnace reductant: An alternative use of waste plastics that is considered as feedstock recycling in Germany is to use the plastics as a replacement for heavy oil as a reductant in blast

furnaces. The waste plastic granules are shredded to ~1 mm and injected into the hot zone at the bottom of a blast furnace. The plastic converts to a reducing gas which rises through the furnace, eventually interacting with the iron ore, which is principally Fe_2O_3 , producing Fe metal, H_2O , CO, and CO_2 . The gases leave the furnace as blast furnace gas and some energy can be recovered from the CO component. They encounter the same problems with feeding the plastic as does an entrained flow gasifier, experiencing great difficulty with melting and plugging. Again, it has been suggested that they consider using the KAB M/D process and feeding the liquid product into the blast furnace. One thing the blast furnaces have great difficulty with is zinc, which is present in PVC. It is also present in tires and waste oil, which might limit their use for this application. The largest use of waste plastics as a blast furnace reductant is at Bremer Stahlwerke in Bremen, Germany, where they use 60,000 tons per year of waste plastics.

Additional Points of Interest: A life cycle analysis that compares various types of feedstock recycling of waste plastics to mechanical recycling and incineration to produce electrical power has recently been completed. The study was jointly sponsored by DSD, APME, VKE (Verband Kunststoffherstellende Industrie - Association of Plastic Recycling Industries), and VCI (Verband der Chemischen Industrie – Association of Chemical Industries) and was conducted by investigators at three German universities.⁽¹²⁾ The feedstock recycling options are compared to each other and to landfilling with regard to consumption of energy resources and environmental factors, such as the greenhouse effect. The study assumes that each process has a particular product (oil, recycled plastic bottles, electrical power, etc.) and that landfilling has no product. It then compares the energy consumption and environmental factors by assuming that a given process produces its own product and the other products are produced from conventional sources by standard processes. The KAB, BASF and blast furnace processes are all significantly better than waste incineration to produce electrical power from both the energy consumption and the ecological points of view. Gasification is also better than waste incineration, but is considerably behind the other three options. With regard to mechanical recycling, much depends on the substitution factor, which is 1 if 1 kg of mechanically recycled plastic replaces 1 kg of virgin plastic. If the substitution factor is close to 1, mechanically recycling is very good energetically and environmentally. However, it is only for a relatively small part of the plastic waste stream, such as uncolored HDPE and PET bottles, that this is true. For the mixed waste plastic that is processed by the feedstock recycling industry, the substitution factor is significantly less than 1 and mechanical recycling becomes energetically, ecologically and economically impractical.

The people who run the processing and preparation plants are unhappy about the fact that most of the money collected by DSD goes to waste management companies that carry out the collection and separation of the waste plastics. DSD collects approximately 3,000 DM/ton, of which approximately 2,000 DM/ton pays for collection and separation, while 400-600 DM/ton is paid to the companies that carry out preparation (shredding and agglomeration) and 400-600 DM/ton goes to the processing companies.

There is little or no problem with waste tires in Germany. This is because Germany has strict laws requiring that tires be removed from cars when they have any less than about 3/8 of an inch of tread. Consequently, used German tires are rather high in quality and they are easily sold to Eastern Europe and third world countries.

The DSD is now close to meeting the requirements of the German legislation of collecting 80% of waste packaging and recycling 80% of the material collected. With regard to feedstock recycling of waste plastics, next year DSD will collect more than 500,000 tons of waste plastics and perform feedstock recycling on over 300,000 tons of this material.

IV. Feedstock Recycling Activity Elsewhere in Europe:

In addition to the above visits in Germany, visits were also made to the Director of the Association of Plastic Manufacturers in Europe (APME), Fred Mader, in Brussels, Belgium, and to a small pilot plant operated in Grangemouth, Scotland by BP Chemicals (Appendix B).

APME has about 40 member companies. They are similar to the American Plastics Council in the U.S. They sponsor about \$2.5 million dollars worth of research per year and contribute to the support of the BP pilot plant in Scotland. At this time, no recycling laws exist in Europe except in Germany. However, similar laws are under discussion in France, Austria, and England.

Mader emphasized that community support, collection and sorting are major keys to success in feedstock recycling of plastics. However, he did not feel that the German yellow bag system is the ideal way because they do not separate plastics from other packaging. Regarding other waste materials, he felt that tires would probably end up primarily in cement kilns. Automobile fluff, electronic waste materials, and construction demolition materials - which contain lots of PVC - are candidates for feedstock recycling. However, there is no legislation on these materials yet and this is the driving factor.

Dr. David Wilson and Steve Hardman hosted a visit to the BP pilot plant at BP Chemicals in Grangemouth, Scotland. BP has adopted a fluid bed reactor because they are familiar with fluid bed technology. One of their principal consultants, Walter Kaminsky of the University of Hamburg, has carried out rather extensive research on the fluid bed pyrolysis of waste plastics.⁽¹³⁻¹⁵⁾ They like the fluid bed because it is very robust, handles solids easily, and produces almost no carbonaceous residue. Their feedstock at this time is the same agglomerated plastic supplied by DSD to the feedstock recycling plants in Germany.

The reactor handles about 100 kg per hour. The plastics are reacted in a fluid sand bath at ~500 °C for residence times of ~1 minute. The reactor is a pipe about 1.5 foot in diameter and about 15 feet high. The pyrolysis products pass through a guard bed containing CaO that removes the Cl as CaCl₂. Solid residues, such as Al foil, tend to clog up this guard bed after a period of time. In larger scale plants, BP plans to add limestone directly to the fluidized bed. Process gas is used to fluidize the bed and also to heat the reactor and fuel the whole process. The product is basically a wax. It is solid at room temperature, but is never cooled in the process. The wax can be used as a feedstock for steam crackers, which produce ethylene and other light olefins, or to refinery units, such as a fluidized catalytic cracker, which produces gasoline and light olefins.

The BP pilot plant is funded by APME and a consortium of companies from different countries: BP,

Fina (Belgium), Elf Atochem (a division of Elf Aquitaine, France), Enichem (Italy), and Dutch State Mines (Holland). A more detailed description of the plant is given in Appendix B.

V. Research Summary

Research on the conversion of waste plastics and tires into oil and on the coprocessing of these waste polymers with coal, resid and waste oil has been quite active for the past 4-5 years. Most of the work has focused on direct liquefaction or hydrotreatment of these feedstocks. In the current section, this research is briefly summarized. Bench scale research has been conducted by the Consortium for Fossil Fuel Science (CFFS), a five university research consortium (University of Kentucky, University of Pittsburgh, University of Utah, West Virginia University and Auburn University) and the in-house research group at the U.S. DOE Federal Energy Technology Center (FETC) in Pittsburgh. Larger scale, continuous experiments and one pilot scale run have been carried out at Hydrocarbon Technologies, Inc. (HTI). Specialized analytical studies have been carried out at Consol, while Mitre Corporation has performed preliminary economic analysis. Recent research in the U.S. has been summarized in several conference and symposia proceedings volumes.⁽¹⁶⁻¹⁹⁾ A recent IEA review of research on the coprocessing of wastes with coal by a variety of processes has been prepared by Davidson.⁽²⁰⁾ As previously noted, a considerable amount of research and development has also taken place in Germany.^(10,13-15,21)

Plastics: Liquefaction of plastics alone has been investigated for individual resins (polyethylene, polypropylene, polystyrene, etc.) and for several mixed or commingled plastics. The latter have included artificial mixtures of specific individual resins and commingled post-consumer plastics provided by the American Plastics Council (APC) and the Duales System Deutschland (DSD). Some of the more interesting results are summarized below, with emphasis on the results for commingled plastics.

A significant amount of research has been conducted on the catalytic liquefaction of plastics. Generally, the best results have been obtained using solid acid catalysts. In early work, HZSM-5 was found to give significant enhancements in oil yields for high-density polyethylene (HDPE), low-density polyethylene (LDPE), milk jugs, soft drink bottles, and mixed waste plastics in the presence of a tetralin solvent.⁽²²⁾ A variety of solid acid catalysts have subsequently been tested for the liquefaction of commingled waste plastics, individual polymers and model mixtures of polymers with no solvent and with waste oil or petroleum resid as a solvent. These include HZSM-5 and other zeolites, silica-alumina, titania-silica, titanium chloride, sulfated and tungstated zirconia, nanoscale iron oxides promoted by sulfate or secondary metals, various supported transition metal catalysts and a number of metal-promoted solid acid catalysts.⁽²³⁻³⁷⁾ Two types of commingled post-consumer plastic have been investigated: a relatively clean plastic provided by the APC that had been subjected to a washing process; and a processed but considerably dirtier post-consumer plastic provided by the DSD. The latter sample was supplied to the CFFS in the same granular form used by the KAB liquefaction plant and other feedstock recycling plants in Germany. The chemical compositions of these two plastics are compared in Table 4. It is seen that the chlorine, ash and

oxygen contents of the DSD plastic are considerably higher than those of the APC plastic. The

decreased chlorine and oxygen contents of the washed APC plastic reflect the removal of PVC, PET and paper by the washing process.

Table 4. Proximate and ultimate analyses of the APC and DSD waste plastics (wt. %).

Proximate	APC	DSD	Ultimate	APC	DSD
Volatile matter	98.8	93.8	C	84.7	79.0
Fixed carbon	0.74	1.08	H	13.7	13.5
Ash	0.45	4.44	N	0.65	0.67
Moisture	0.01	0.16	S	0.01	0.08
			Cl	0.03	1.26
			O (difference)	0.91	5.49

Direct liquefaction experiments have been conducted the APC plastic as a function of temperature, hydrogen or nitrogen pressure, and solvent (no solvent, waste oil, tetralin, and waste oil-tetralin mixtures).⁽²³⁻³⁰⁾ Liquefaction yields at 430-450 °C under low hydrogen pressures (100-200 psig, cold) or under nitrogen were not markedly different than those under high hydrogen pressures (800 psig, cold). The best results were obtained with no solvent or with an aliphatic solvent such as waste oil. Addition of 1-4 wt.% of a variety of catalysts (HZSM-5 and other zeolites, silica-alumina, titania-silica, titanium chloride, sulfated and tungstated zirconia, nanoscale iron oxides promoted by sulfate or secondary metals) had a significant beneficial effect on oil yields at temperatures \leq 430 °C, but marginal effect at higher temperatures. At 445 °C, the oil yield was over 80% for both thermal and catalytic liquefaction using all of the catalysts noted above at low concentrations (1-several percent). However, the catalysts did have a beneficial effect on the quality of the oil derived from the APC plastic as determined by simulated distillation and GC-MS. Similar experiments using the DSD plastic^(29,30) again established that both the thermal and catalytic (1 wt.% of above catalysts) oil yields were over 80% at 445 °C. In this case, however, there was little or no effect on oil quality, presumably because of catalyst poisoning.

Larger catalytic effects are observed using higher concentrations of bifunctional catalysts at lower temperatures. Studies of the depolymerization-liquefaction of polyethylene, polypropylene, polybutadiene, polystyrene, and styrene-butadiene were carried out by Shabtai⁽³¹⁻³³⁾ and coworkers using the superacid catalysts $\text{SO}_4^{2-}/\text{Fe}_2\text{O}_3$, $\text{SO}_4^{2-}/\text{ZrO}_2$, and a Pt-promoted $\text{SO}_4^{2-}/\text{ZrO}_2$ at catalyst concentrations of 17-33%. The results obtained using the Pt/ $\text{SO}_4^{2-}/\text{ZrO}_2$ were significantly better than those for any other catalyst, giving gasoline yields of over 70% at temperatures of only 350 °C and hydrogen pressures of 700-900 psig. Promising results were also obtained from catalysts consisting of sulfided transition metals on silica-alumina supports, which combine both hydrogenation and hydrocracking functions. A carbonium ion mechanism is proposed for the catalytic depolymerization reaction. Venkatesh et al.^(34,35) found metal-promoted, sulfated or tungstated zirconia catalysts to be highly active for hydrocracking of HDPE. Using Pt or Ni promoted ZrO_2/SO_4 or ZrO_2/WO_3 at concentrations of 17%, the liquid products obtained from HDPE and PP at 375 °C, 750-1200 psig hydrogen (cold), were over 85% in the gasoline range. Although the results obtained using Pt or Ni promoted, sulfated or tungstated, zirconia catalysts for liquefaction of polyethylene, polypropylene and other pure polymers are impressive, the catalysts

are not effective with post-consumer commingled plastics, presumably because they are easily poisoned by heteroatoms and other species. Shabtai and coworkers, however, have developed solvent pre-treatment methods to remove O- and N-containing polymers that render commingled plastics susceptible to low severity liquefaction using these catalysts.⁽³⁶⁾

Ding et al.⁽²⁷⁾ have been successful in carrying out catalytic liquefaction of the APC commingled plastic at 375 °C. Using 20 or 40% additions of sulfided Ni or NiMo supported on silica-alumina or silica-alumina/HZSM-5, they achieved oil yields of 40-65%, as compared with a thermal liquid yield of only 8% at that temperature. Furthermore, the oil was quite high in quality, having a boiling point distribution similar to commercial gasoline and containing more isoparaffins, less aromatics and < 0.01 % N and S. For the DSD plastic at a higher temperature (400°C) using 20% of similar catalysts, they observed oil yields of 40-50%, as compared to a thermal oil yield of 25%.⁽²⁸⁾

Research on pyrolysis of post-consumer plastics has been carried out by Kaminsky and coworkers,⁽¹³⁻¹⁵⁾ by Conrad Industries,⁽³⁸⁻⁴⁰⁾ and Shah et al.⁽⁴¹⁾ within the CFFS program. Kaminsky et al.⁽¹³⁻¹⁵⁾ employ a fluid bed pyrolysis reactor in the temperature range 700-750 °C with a residence time of several seconds. The fluidizing material is sand, the gas is pyrolysis gas generated in the process, and lime is added to capture the Cl liberated from PVC as HCl. Pyrolysis gas is also used to fuel the process. For feedstock, they have used individual polymers and commingled post-consumer plastics (PCP), such as the DSD plastic discussed earlier. They have also used density separation in a salt water medium (density, 1.17 g/cc) to remove polyvinylchloride (PVC) and dirt from PCP. The uncleaned PCP they used contained 7.4 wt.% Cl, while the cleaned PCP contained 0.7 wt.% Cl. At a temperature of 730 °C for the cleaned PCP, they observed yields of 49% oil, 35% gas, and 17% residue, with predominantly aromatic oils (45%) and a Cl concentration in the oil of 4 ppm. Under the same conditions, the uncleaned PCP gave yields of 29% oil, 49% gas, and 21% residue, with 25% aromatic oils, 4% aliphatic oils, and 400 ppm Cl concentration in the oil.

Conrad Industries has conducted extensive studies on individual polymers, blends of pure polymers, and PCP using an auger-driven pyrolysis system that typically processed ~100 lbs. of material per hour. For various blends of pure polymers (PE, PP, PS, etc.) they have reported yields of liquid products generally in the range of 50-70%.⁽³⁹⁾ For the PCP data reported in their final report to the American Plastics Council,⁽³⁹⁾ they used feedstocks from a number of recycling centers that had experienced various types of cleaning. Consequently, the four PCPs they investigated contained relatively little PVC (0 - 1.5%) and little dirt or paper. Relatively low pyrolysis temperatures were employed, from 500 to 590 °C. No solid residue yields were given, with the oil + gas yields normalized to 100%. For third bale plastics, based on the German experience (Appendices B and C) and the experimental work by the CFFS, FETC, HTI and others, the solid residue from either liquefaction or pyrolysis of real third bale, post-consumer waste plastic is likely to be 10% or higher. In order to compare the Conrad PCP results with the others discussed in this report, it is therefore assumed that their reported normalized oil and gas yields should be corrected for the ~10% solids that would be produced by third bale plastics containing significant amounts of paper, dirt, aluminum foil, etc. On this basis, the corrected Conrad PCP oil yields would vary from approximately 28 to 54%, while the gas yield would range from 36 to 62%, with the oil yield increasing and the gas yield decreasing with decreasing temperature.

Recent work by the CFFS indicates that pyrolysis in a closed reactor followed by hydroprocessing is a good method of converting dirty post-consumer plastic, such as the DSD plastic, into high quality oil products. Shah et al.⁽⁴¹⁾ have carried out pyrolysis experiments on the DSD waste plastic as a function of temperature in a batch mode reactor. The pyrolysis retort is initially flushed with nitrogen, but is soon filled with self-generated gases as the plastic begins to decompose. As shown in Figure 2, liquid yields approaching 80% are obtained at furnace temperatures of approximately 600°C and residence times of an hour. During the one hour residence time, the temperature of the sample is continually increasing as heavier and heavier molecular components reach their boiling points and are released. Typically, the sample temperature is 50-100 °C below the furnace set point temperature (shown in Figure 2) at the end of an hour. The simdist results, shown in Figure 3, show that the pyrolysis liquids obtained at the temperatures of maximum oil yield are relatively heavy. However, Figure 3 also illustrates that hydroprocessing them either thermally or catalytically converts them into a much lighter product. The hydroprocessing conditions were 200 psig hydrogen (cold pressure), 60 min. reaction time in a 50 ml tubing bomb microreactor at 450 °C, with either no catalyst added or with 1 wt.% HZSM-5. Addition of sodium carbonate or lime to the pyrolysis and hydroprocessing reactors reduces the chlorine content of the pyrolysis liquids to ~50-200 ppm, and that of the hydroprocessed oils to ~1-10 ppm.

Coprocessing of plastics with coal: Coprocessing or coliquefaction of plastics with coal has been studied as a function of temperature, catalyst, pressure and time. Some the results are briefly summarized below.

Both bituminous coal (Blind Canyon seam, DECS-6) and subbituminous coal (Black Thunder) have been coprocessed successfully with a mixed waste plastic.⁽²²⁾ Good results were obtained using a tetralin solvent, a 1:1 mixture of plastics and coal, and 1% additions of HZSM-5 and a nanoscale iron oxide catalyst. For the bituminous coal-plastic mixture, the oil yield was approximately 60% and the total conversion approximately 80%. For the subbituminous coal-plastic mixture, the oil yield and total conversion were 70 and over 90%, respectively. The experiments were carried out at 430 °C under high pressure hydrogen (800 psig, cold). Under similar conditions, it was observed that a 1:1 mixture of PPE and subbituminous coal gave significantly higher yields than a 1:1 mixture of PE and subbituminous coal.⁽²⁴⁾ These results can be explained by a molecular model of the interaction of coal-like molecules with either PE⁺ or PPE⁺ using the tight binding approach.⁽⁴²⁾

SiO₂-Al₂O₃, promoted by addition of Fe, Pd, Pt, and Ni, was used to catalyze the liquefaction of 1:1 mixtures of Blind Canyon coal with commingled waste plastic and high density polyethylene.⁽²⁵⁾ Ni/SiO₂-Al₂O₃ gave the best results, with oil yields of over 60% and total conversions of over 80% at 450 °C, 2000 psig hydrogen. An autoclave reactor gave better results than a tubing bomb reactor.

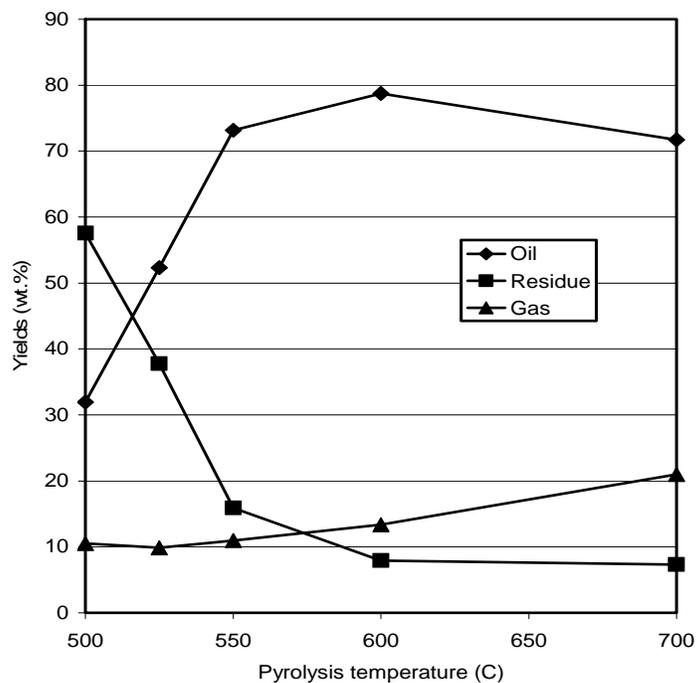


Figure 2. Oil, gas, and residue yields from DSD plastic as a function of pyrolysis temperature.

A two-stage coprocessing method for plastics and coal was developed.⁽²⁵⁾ Plastics are first liquefied under nitrogen at ambient pressure using a TiO_2 or a metal (Pt, Pd, Ni)-promoted TiO_2 catalyst; the liquid product is then combined with coal impregnated with Fe and liquefied under high pressure hydrogen. Oil yields of 35-50% and total conversions of up to 90% are observed for a bituminous coal (DECS-6). In a second set of experiments, both a commingled waste plastic and HDPE were first liquefied at 435 °C under either nitrogen (ambient pressure) or hydrogen (1000 psig, cold), with or without addition of 2 wt.% HZSM-5. The resulting plastic-derived liquids (PDL) were then used as solvents for liquefaction of DECS-6 coal at 400 °C, ~2000 psig hydrogen; both noncatalytic and catalytic liquefaction of the coal using 1 wt.% of impregnated iron catalyst was investigated. The catalytic liquefaction of DECS-6 coal using the PDL as solvent gave good results, comparable to those obtained using tetralin as the solvent, with the best total conversion and oil yields resulting from the use of PDL solvents produced using HZSM-5.

Research conducted by Curtis and coworkers⁽⁴³⁻⁴⁹⁾ has investigated several approaches for the coprocessing of plastics, rubber, coal and petroleum resid. The effect of reaction time was determined for liquefaction of LDPE, LDPE + coal (DECS-17, Blind Canyon) - 1:1 mixture, and LDPE/coal/Maya resid - 1:1:1.5 mixture. Conditions were 8.3 Mpa hydrogen, 430 °C, 1 wt.% NiMo/ Al_2O_3 . Total conversion and hexane solubles increased steadily from times of 60 minutes

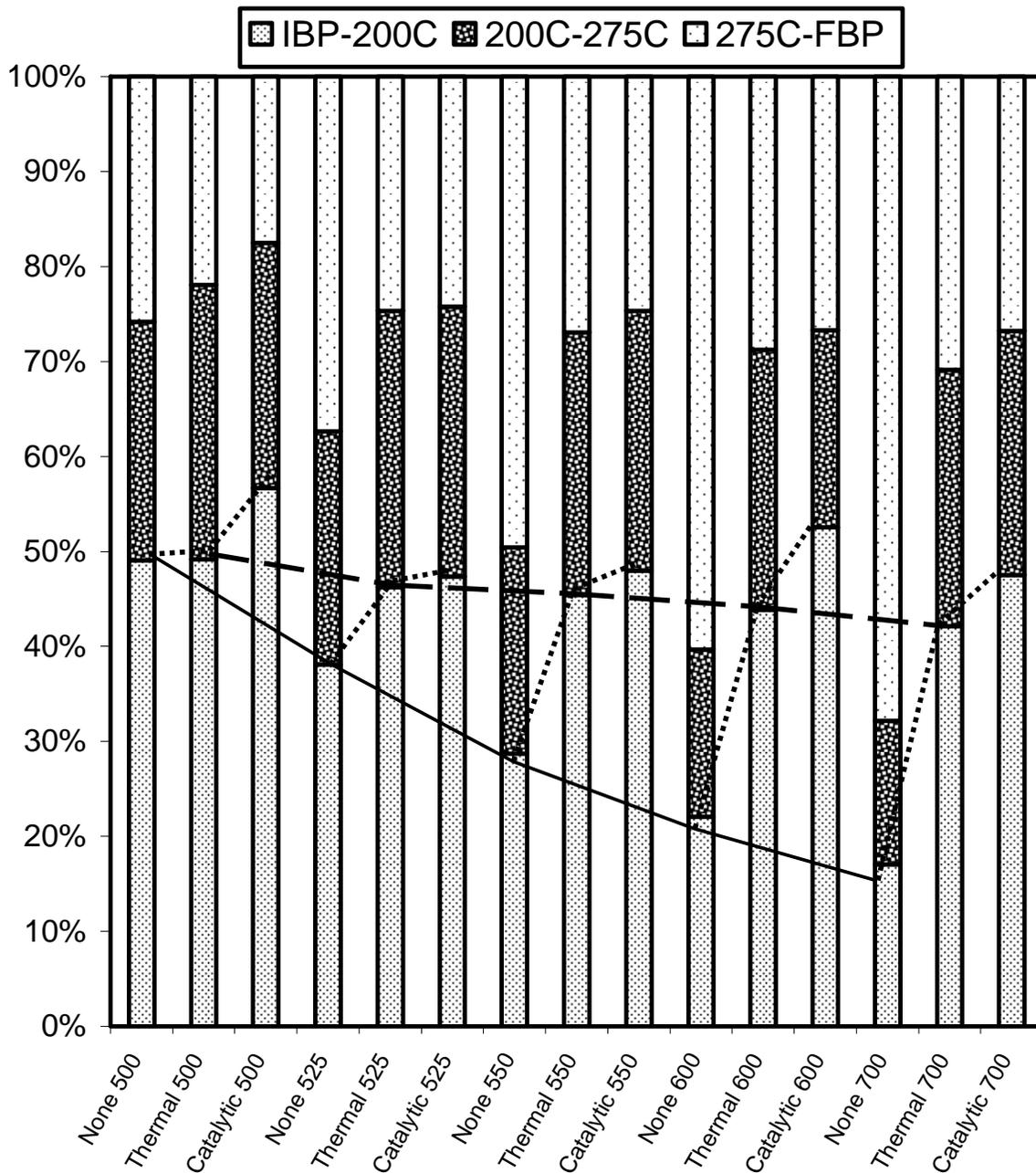


Figure 3. Simdist analysis of pyrolysis oil from DSD waste plastic before and after thermal or catalytic hydroprocessing.

to 300 minutes. For the LDPE/coal/resid mixture, the total conversion and oil yield increased from 77 and 53%, respectively, at 60 minutes to 88 and 67% at 300 minutes. The effect of several

catalysts on the liquefaction of LDPE and the coprocessing of LDPE with coal and petroleum resid was also investigated. The catalysts included NiMo/Al₂O₃, NiMo/zeolite, and Z-753. It was concluded that the best results for LDPE alone were produced by hydrocracking catalysts, while the highest oil yields and total conversions for the LDPE/coal/resid system resulted from catalysts with both hydrocracking and hydrogenation activities, such as NiMo/zeolite or a mixture of NiMo/Al₂O₃ and Z-753. Two stage coprocessing of waste plastics and coal and tire rubber and coal was also investigated; in these experiments, the liquid products from either plastics or rubber were used as the solvent for coal liquefaction. For the waste plastic-coal two stage process, a hydrocracking catalyst was used in the first stage and 500-1000 ppm of Fe and/or Mo naphthenate was used in the second stage. In the study using liquid from the tire rubber as the second stage solvent, either Mo naphthenate or sulfided NiMo was used as the second stage catalyst. For the plastics-coal two stage coprocessing, total conversions of 70-90% and oil yields of 30-40% were obtained. The rubber-coal two stage coprocessing experiments achieved total yields of 80-95% and oil yields of over 50%. Two stage experiments were also conducted using liquids derived from the DSD plastic and other plastics, resid and coal with a number of different catalysts. The observed oil yields were 50-75% with no coal present and 40-60% with 10-30% of coal. ⁽⁴⁹⁾

Depolymerization of individual polymers, both alone and combined with coal, has been studied under coal liquefaction conditions. ⁽⁵⁰⁾ Polystyrene (PS) was found to yield primarily alkybenzenes, especially ethylbenzene. Polyethylene (PE) and polypropylene (PP) were found to yield aliphatic hydrocarbons, with depolymerization of PP much easier than PE. Polyethylene terephthalate (PET) was found to yield benzene, carbon dioxide and ethane, with terephthalic acid formed as an intermediate breakdown product. Conversion of HDPE to low molecular weight species required higher temperatures than the other polymers, consistent with the lack of reactive sites in its structure. A procedure for extraction of incompletely reacted PE from coprocessing product streams was developed and applied to samples obtained from a 50 lb/day continuous reactor at HTI. ⁽⁵¹⁾ The recovered samples were analyzed by gel permeation chromatography. Rapid initial breakdown of PE reduces its molecular weight by a factor of 10-30, but further molecular weight reduction occurs more slowly.

Wender and co-workers have carried out coprocessing experiments on mixtures of plastic with coal and plastic with paper using the COSTEAM process. ⁽⁵²⁾ In this approach, the reactor is charged to a relatively high pressure with CO and H₂O and alkali is added as a catalyst. While the total conversions obtained are high, the gas yields are usually somewhat excessive.

Larger scale coprocessing studies on coal and plastic have been carried out by Hydrocarbon Technologies, Inc. (HTI). One three ton per day pilot scale run and a number of continuous runs using a 50 lb/day continuous reactor have been conducted with a model mixture of polymers (HDPE, PPE, and PS) and with a post-consumer mixed waste plastic. Catalysts used have included a conventional hydrogenation catalyst, NiMo/Al₂O₃, and nanoscale iron-based catalysts. Generally, the results of these runs have been quite good and have confirmed results obtained on a smaller scale in the laboratory. Recent summaries of this work have been given by Pradhan et al. ⁽⁵³⁾ and by Lee et al. ⁽⁵⁴⁾

Rubber:

It has been known for some time that the pyrolysis of tire rubber at temperatures in the range from approximately 600 to 800 °C yields a volatile oil product, some gas, and a residue consisting primarily of carbon black and inorganic tire additives, such as steel wire and zinc oxide. ^(55,56,13) Yields depend on the nature of the pyrolysis process, but generally they are in the following ranges: oil – 40-50%; gas – 10-20%; and solids – 30-40%. The problem with pyrolysis alone is that the oil is aromatic, high in sulfur and somewhat unstable, while the carbon black has low surface area and contains a relatively high ash content, making it unsuitable for reuse in tires or for other purposes. The thrust of the current program has therefore been to derive high quality products by catalytic hydroprocessing of the liquid and activation and upgrading of the carbon black.

The initial work on coprocessing of tire rubber with coal was carried out by Farcasiu and Smith. ^(57,58) They conducted experiments on mixtures of bituminous coal and crumb rubber at a temperature of 400 °C under high pressure (1000 psig, cold) hydrogen. Their results indicated that the hydrocarbon polymeric fraction of the rubber was converted to oil, while the oil yield from the coal was enhanced by catalytic activity of the carbon black.

Subsequent experiments by Dadyburjor, Zondlo, and coworkers ⁽⁴⁶⁻⁵⁰⁾ and by Eyring, Anderson and coworkers. ⁽⁵¹⁻⁵⁴⁾ These investigators have examined the hydrotreatment of rubber alone and the coprocessing of coal with crumb rubber and oil derived from rubber as a function of temperature, hydrogen pressure, and catalyst. The optimum temperature range for liquefaction of tires alone or for coprocessing of tires with coal was found to be approximately 400-420 °C. For tires alone, as in the case of plastics discussed above, high pressure hydrogen is not needed; high oil yields (55-60%) are obtained either under low pressure hydrogen (100-200 psig) or under nitrogen. The coprocessing studies were carried out as a function of pressure and as a function of the coal to rubber ratio using several different hydrogenation catalysts, including a dispersed Mo catalyst and a dispersed nanoscale iron catalyst. The results may be summarized as follows:

1. The rubber converts in essentially the same way as it does when coal is not present, yielding 55-60 % oil, 30-35% carbon black and inorganics and minor amounts of gas. It therefore serves effectively as a solvent for coal liquefaction. Coprocessing of coal with vacuum-pyrolyzed tire oil gave oil yields of approximately 50-70% for coals of various ranks.
2. High hydrogen pressure (~1000-2000 psig) is required for conversion of the coal.
3. No significant synergistic effects are observed as the tire to coal ratio is varied; that is, the total liquid and oil yields are approximately what would be expected on the basis of the yields obtained from the rubber and coal alone.
4. The oil quality is enhanced by the presence of a hydrogenation catalyst.

Recent research has established that the carbon black remaining as a residue after pyrolysis or liquefaction of tires can be significantly upgraded. Merchant and Petrich ⁽⁶⁹⁾ produced carbons with surface areas greater than 500 m²/g by steam activation of tire pyrolysis char. They observe porosity development similar to that found for various other chars. Dadyburjor et al. ⁽⁷⁰⁾ have constructed a rotating tube reactor for activation of carbon black in flowing CO₂ and have investigated ash removal by acid extraction. At 40% burnoff, they have produced carbon products with surface areas of 400-800 m²/g and ash concentrations of only 0.5-2.0 %. Allen et al. ⁽⁷¹⁾ have activated carbon black derived from pyrolysis of tires and investigated possible environmental applications.

Specifically, they have measured butane working capacity (BWC), of interest with regard to adsorption of volatile organic compounds, and the capture of mercury from the vapor phase. They have achieved a BWC approximately 50% of that exhibited by a commercial wood-based activated carbon. They have also obtained promising results for “mercury breakthrough” using an activated and sulfided carbon black.

VI. Availability of Waste Polymers

Early in its discussions, the feasibility study committee decided that a reasonable size for a first demonstration plant would be approximately 200 tons per day (t/d) of plastics and 100 t/d of tires. Since several members of the committee expressed concern over whether this quantity of waste material would be easily available, it was decided that a survey of one of the areas being discussed as a possible plant location would be appropriate.

The survey was conducted by Michael A. Mills, President of the Bluegrass Regional Recycling Corporation (BRRC) located in Lexington, KY. Mr. Mills conducted a survey of potential suppliers of waste plastics and tires in an eight-state area within a 300 mile radius of Lexington. The survey included a written questionnaire mailed to 5,000 potential waste polymer suppliers to which 200 recipients responded, a number of on site visits, and a phone survey. The eight states within the 300 mile radius survey region included Kentucky, West Virginia, Tennessee, Ohio, Indiana, Illinois, Georgia and Virginia. Mr. Mills’ report ⁽⁷²⁾ is included as Appendix D to this report. A brief summary of his findings is given below, categorized by type and source of waste material.

Used tires: Every state in the survey has a problem disposing of used tires. Use of tires as tire derived fuel (TDF) is practical only in a few states, most notably Georgia, where TDF is widely used in paper mills. The use of crumb rubber as an asphalt additive is limited and is expected to decrease as a result of recent changes in Federal legislation. The current investigation concluded that approximately 75% of all used tires in the study area are landfilled, stockpiled, or illegally dumped. Currently, there are approximately 10 million tires “on the ground” in Kentucky, 12 million in Ohio, 15 million in Indiana and 2 million in Georgia. The lower number in Georgia reflects the use of tires as TDF in paper mills.

Automobile and Appliance Shredder Residue: Automobile and appliance shredder residue (ASR) or “shredder fluff” consists of plastics, rubber, grease, oil, glass and dirt. New cars produced in the U.S. contain an average of 365 pounds of plastics and this is increasing. Approximately three billion pounds of plastics were used in automobile production in 1996. There are 29 auto shredding companies in the study area. Appliances are a relatively new addition to the shredding industry; they account for seven percent of the shredder fluff. Currently, shredder fluff accounts for two percent of landfill usage at an average disposal cost of \$30/ton. The amount of shredder fluff produced in the study area is estimated to be 548 t/d.

Bedminster Bioconversion Corporation: Bedminster Bioconversion Corporation (BBC) has developed a patented biological digestion technology that converts some types of waste into humus, a component of topsoil. BBC has two plants in the study area, located in Sevierville, Tennessee, and Marietta, Georgia. These two plants accept over 500 tons of municipal solid waste (MSW) daily.

Much of the unconverted residue from the process is plastic and rubber (~50 t/d). Currently, BBC is paying over \$30 per ton to dispose of this material in landfills and they are anxious to find an alternative solution.

MRFs and Co-ops: Municipal recycling facilities (MRFs) and recovery co-ops throughout the study area were contacted. MRFs and co-ops are facilities that divert recyclable waste materials from landfills to markets. Currently, the only waste plastics being diverted for recycling are PET and HDPE bottles and containers. In the waste plastic classification terminology, these items are referred to as 1's and 2's. All other types of waste plastics are numbered 3-7; they are normally baled and disposed of in landfills and are referred to as the "third bale". The current study concludes that approximately 85,000 tons per year (t/y) of third bale plastics from the eight-state study area within 300 miles of Lexington are disposed of in landfills.

Plastic and tire industry: The plastic industry generates a significant amount of waste material that must be recycled or disposed of. Ohio is the second largest plastic producer in the nation, while Indiana is the second leading plastic manufacturer in the study area. There are 4,574 plastic manufacturing companies in the study area and a significant number of tire manufacturers. The current survey of 5,000 companies drew 146 responses, all of which reported waste plastics, rubber or both to discard. Over 80 percent indicated they would be favorable to contributing waste plastic and rubber to a liquefaction plant. The 146 respondents indicated over 7,000 t/y of waste plastic and rubber. Therefore, a reasonable estimate of the waste plastic/rubber in the study area for all manufacturers is over 200,000 t/y.

Carpet industry: Almost all discarded carpet ends up in landfills. Carpet accounts for 1% by weight and 2% by volume of MSW in the U.S., equivalent to 2,000,000 t/y. Carpet face fibers, which are 40-60% of the total carpet weight, consist of approximately 70% nylon, 20% polypropylene, and 10% polyester. The largest concentration of carpet waste in the study area is in the Dalton-Whitfield area in Georgia, where a carpet monofill collects most of the waste carpet from the 177 carpet manufacturers in that state. Currently, the monofill contains over 200,000 tons of waste carpet and it is being added to at the rate of 50,000 t/y.

Paper mills: Paper mills, which are abundant in the study area, produce a waste referred to as pulper trash, which is predominantly plastic and rubber. One producer, Inland Container, produces 60 t/d. A liquefaction experiment on this material conducted at the University of Kentucky yielded over 70% oil, about 15% gas and 10% solid residue.

Conclusions of the survey on waste tire and plastic availability: The situation with regard to tires is fairly clear. A plant using 100 t/d of tires or 10,000 tires a day will utilize about 3.5 million tires a year. Within the 300-mile radius study area, approximately 15 million tires are disposed of each year and there are tens of millions of discarded tires "on the ground". It is therefore anticipated that there would be little difficulty in obtaining the tires need for a demonstration plant in this area.

The available supply of waste plastic in the study area also looks encouraging but the situation is more complex. On the basis of nationwide surveys,^(1,2) it can be estimated that over a million tons per year of post-consumer waste plastic being generated by the 15,000,000 population base in the

study area. However, only 85,000 t/y are currently being separated into the third bale plastic feedstock that would be processed by the demonstration plant. The total waste plastic from all of the sources surveyed (MRFs and co-ops, automobile and appliance shredding companies, BBC, plastics and tire manufacturers, carpet manufacturers and paper mills) amounts to over 500,000 t/y in the study area. However, it should be noted that relatively little research has been completed on the liquefaction/hydrotreatment of shredder fluff, carpets, or residue from operations such as paper mills and the BBC. Consequently, the primary supply of waste plastic within the study area for which the technology base is well established is approximately 285,000 t/y. A demonstration plant processing 200 t/d or approximately 70,000 t/y of plastic would require 25% of that material. In view of the fact that the chosen study area has a relatively low population density, these results are considered promising. Nevertheless, they suggest that it would be prudent to establish contracts with MRFs, co-ops and plastic manufacturers to acquire their waste plastic prior to designing a demonstration plant for a particular region.

VII. Conceptual Design of the Demonstration Plant

A modular design was decided on by the committee as the base design for the demonstration plant. The base design is illustrated by the flowsheet in Figure 4. It consists of a plastic module, a tire module, and an upgrading module. The diagram also allows for feeding waste oil and petroleum resid to the upgrading module and coal to the pyrolysis unit of the tire module.

The motivation behind the modular design is to allow a firm to develop one or several modules, according to its particular needs. For example, it may be desirable under certain circumstances to operate either the plastic module or the tire module alone.

Tire module: Focusing first on the tire module, the committee felt that it would be impractical to attempt to process the whole tire through the plant because of the high content of carbon black and steel wire. Consequentially, it seemed reasonable to make pyrolysis the first processing step. As noted earlier, this produces about 40-50% pyrolysis oil, which leaves the pyrolysis system as a volatile component, leaving behind the carbon black and wire. An Auger fed pyrolysis unit, of the type developed by Conrad industries, would seem well suited for easy recovery of the carbon black and wire. The steel wire is readily separated from the carbon black magnetically, and may be sold as scrap steel for \$40-50 per ton. The carbon black as it leaves the pyrolysis unit has a low surface area and high ash concentration and is of little value. However, as discussed in the **Research Summary** section, it can be activated by partial oxidation in either CO₂ or H₂O and purified by removal of inorganics.⁽⁶⁹⁻⁷¹⁾ Surface areas of 400-800 m²/g and ash concentrations of 0.5-2% have been achieved and there is good potential for a number of applications.

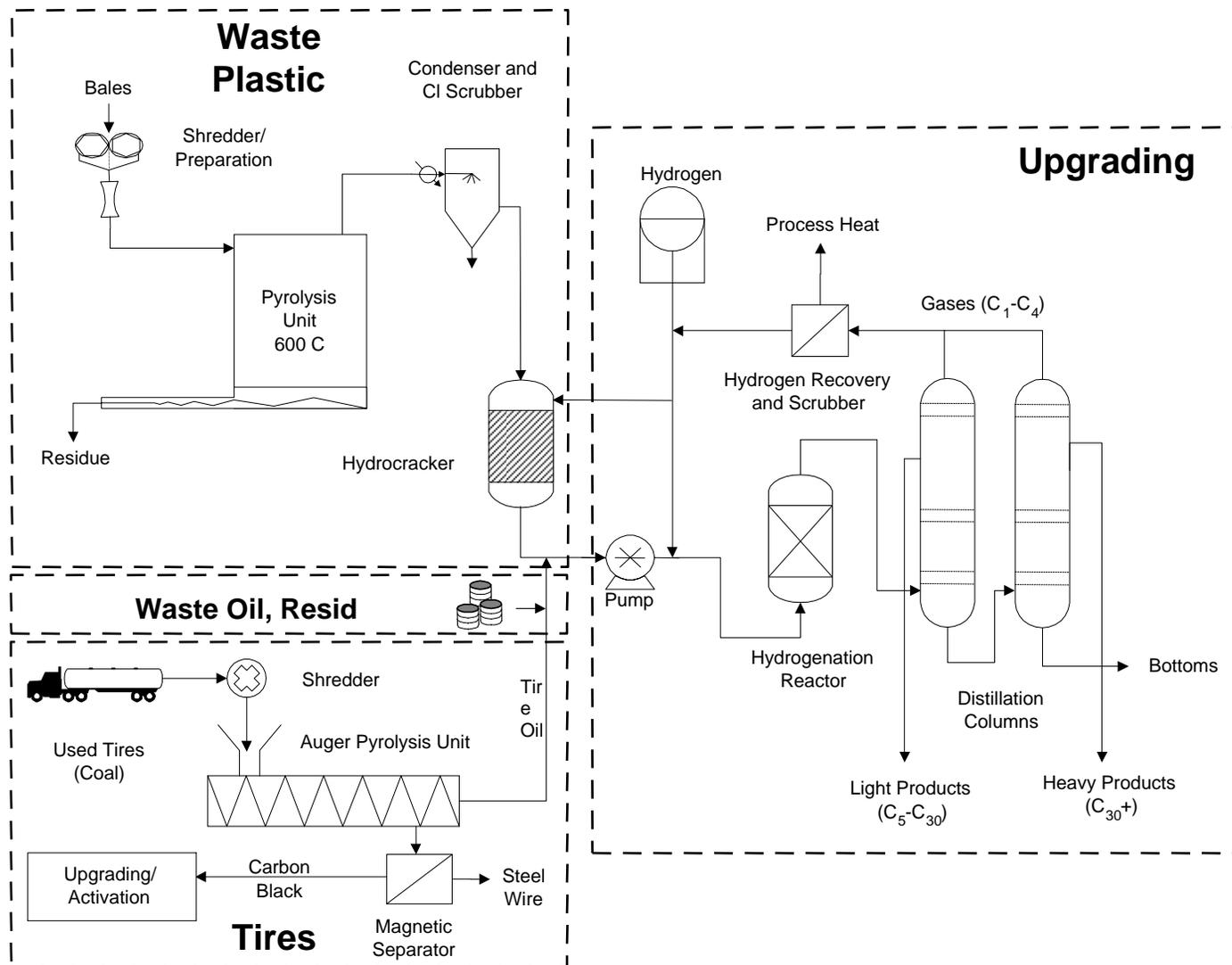


Figure 4. Conceptual design for a demonstration plant for processing of waste plastics and tires, with a pyrolysis-based

Tires may either be delivered to the plant in a shredded form or as whole tires. If the tires are delivered in whole form, the plant can receive a tipping fee of \$0.75-1.00 per tire. However, since pyrolysis units that are currently on the market utilize shredded tires (nominally 2-4 inches in size), this will force the developer to go into the tire shredding business. This would obviously entail additional capital and labor costs. Another option would be to buy shredded tires from companies that are currently in the tire shredding business. Since the current price paid to these companies for shredded tires for use as TDF is \$20-25 per ton, it is reasonable to assume that the demonstration plant could purchase them for the same price. However, it is known from discussions by committee members with personnel in the state Department of Environmental Resources (DER) of the states of Kentucky and West Virginia that it is not unusual for states faced with tire disposal problems to pay \$20-25 per ton to have tires shredded and then to pay an *additional* \$30-40 per ton to place the shredded tires in landfills. Consequently, if agreements could be reached with one or more state DER agencies, it might be possible to receive tires in the desired shredded form at no cost or even be paid to accept shredded tires. For the current study, it was therefore decided that the economic analysis should consider the tipping fee for tires to be a variable, ranging from -\$20 per ton (the plant pays a tire recycling company \$20 per ton for shredded tires) to +\$75 per ton (the plant receives a tipping fee of \$0.75 per tire and does its own tire shredding).

It is worth noting that it is possible to separate the rubber from the wire and nylon cord in the shredding stage if the tires are shredded to much finer size, producing what is usually referred to as crumb rubber (Appendix A). However, the cost of this would be prohibitive, ranging from \$200 to \$1,000 per ton, depending on the final mesh size of the rubber. It was therefore decided that pyrolysis of the 2-4 inch shredded tires to separate the oil from the inerts was a much better option.

Plastic module: Two types of plastic module were considered. The flow diagrams are compared in Figure 5. In one alternative (Figure 5a), melting and partial depolymerization (M/D) of the plastic is carried out at a moderate temperature (~380 °C) over a long residence time (5-6 hours). 20-30% of the material leaves the reactor as light, volatile oils that are scrubbed to remove HCl, condensed, and passed on to the upgrading module. Aluminum foil and other inerts sink to the bottom of the liquid remaining in the M/D reactor and are removed. The aluminum is sold as a by-product. The heavy hydrocarbon liquid remaining in the reactor, which constitutes 60-70% of the plastic, is transferred first to a hydrocracking reactor, then to the upgrading module. This approach is very similar to technology currently in use in Germany (Appendix B and reference 10).

In the second type of waste plastic module, the plastic is subjected to pyrolysis in a closed reactor in a plastic-generated atmosphere at a higher temperature (~600 °C) for a considerably shorter residence time (~1 hour). The volatile product from this process is scrubbed and condensed, yielding about 10-15% gas and 75-80% of a relatively heavy oil product that is transferred first to a hydrocracking reactor, then to the upgrading module. Limestone or a sodium compound is added to the pyrolysis reactor to insure efficient capture of chlorine. As discussed in the **Research Section**, Shah et al.⁽⁴¹⁾ have demonstrated that the chlorine contents of the pyrolysis liquids produced from post-consumer

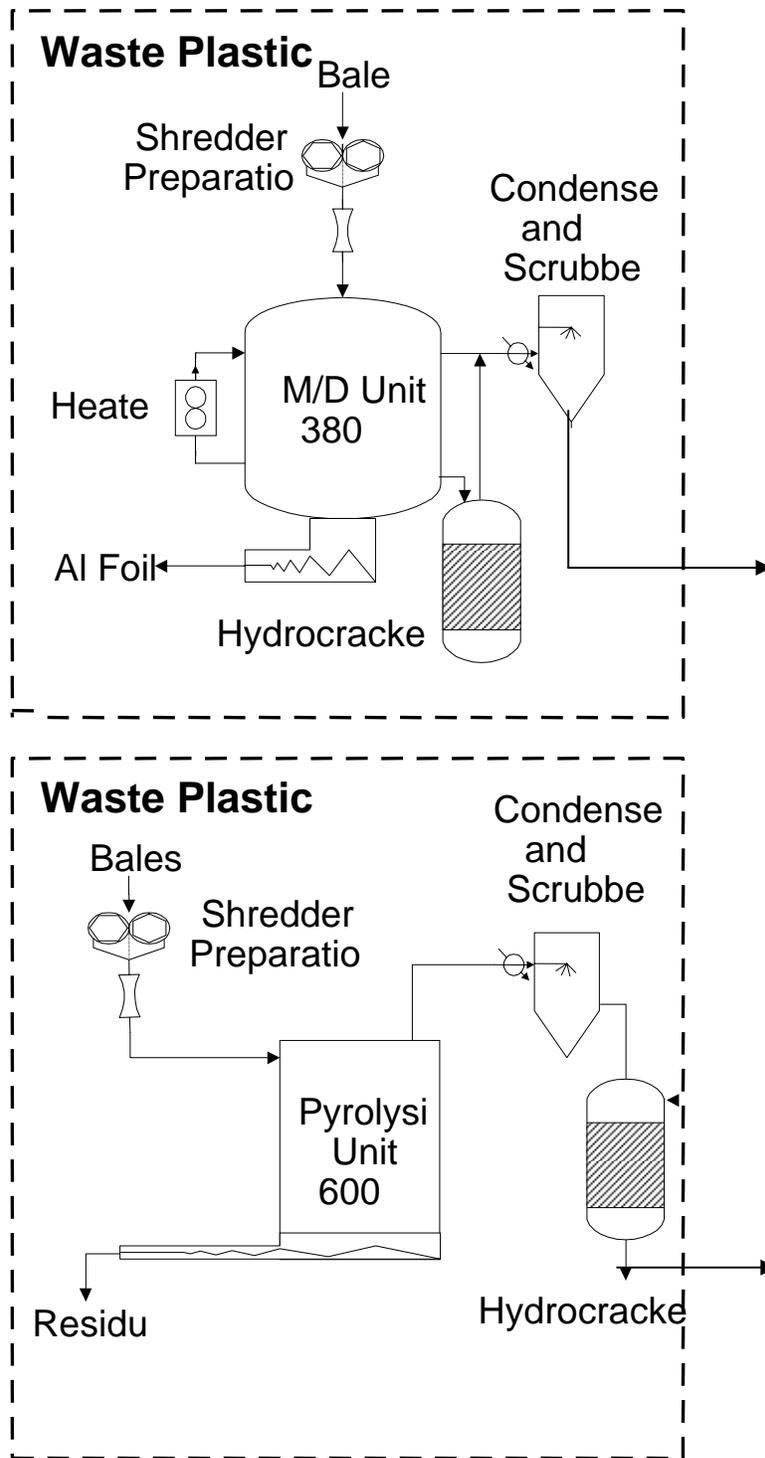


Figure 5. Comparative flow diagrams of alternative plastic modules using a melting depolymerization reactor (top) or a pyrolysis reactor (bottom).

plastic containing >1 wt.% chlorine are in the 50-200 ppm range. Thus, it should be possible to use more economical steel for the hydrocracking reactor than in the case of the M/D reactor where the liquid product contains 1,000-2,000 ppm of chlorine. Additionally, although not indicated in Figure 5, the shredding and preparation steps required to prepare waste plastic for the pyrolysis reactor are much simpler than those required for the M/D reactor.

As discussed earlier in this report (see subsection on Current practice in Germany) and in more detail in Appendix C, the DSD and their contractors have developed plastics sorting and preparation technology that enables them to prepare a very uniform and consistent feedstock for several types of plastic processing plants, including the KAB liquefaction plant in Bottrop. Such technology does not yet exist in this country. Nevertheless, as discussed earlier, there are many MRFs in the U.S. where waste plastics are separated from the municipal waste stream. The material available from the MRFs for a plant of the type under discussion would be third bale waste plastic from which most of the PET soda bottles and HDPE milk jugs have been removed for mechanical recycling. Additionally, there is a great deal of waste material generated in the plastics manufacturing industry. Both types of plastic waste would first be subjected to shredding to a size of ~1-10 cm. Although not specifically shown in the flowsheets, the shredded plastic from the MRFs would also need to be subjected to cleaning processes to remove non-plastic materials (metal, paper, glass, dirt, etc.). Although such separation will have already occurred to some extent at the MRF, there will still be quite a bit of non-plastic material remaining in the third bale. At a minimum, it will be necessary to subject the shredded material to magnetic separation to remove steel and ferrous material and to eddy current separation to remove aluminum. Additionally, as discussed Appendix C, separation of paper and dirt can be accomplished by aeration and screening. In the technology developed under the sponsorship of DSD, multiple cleaning steps of this type are used to achieve the rather stringent product specifications required by the processing plants (see Table 3). Following the shredding and separation steps, the German preparation plants subject the plastic to an agglomeration step, in which it is converted to small (~2-10 mm) granules that are loaded on trucks and shipped to the processing plants. The committee conclusion on plastic preparation was that the pyrolysis reactor would be much more forgiving than the M/D reactor with regard to total inorganic content, paper content and physical uniformity of the feedstock. Consequently, the preparation of the plastic for pyrolysis includes only shredding to sizes ~10-100 mm and single magnetic, eddy current, aeration and screening steps to remove non-plastic material, with no agglomeration process.

As discussed further in the **Economic Analysis** section, the combined factors of less costly materials for the hydrocracker and a simpler, cheaper, plastic preparation process make the pyrolysis plastic module more economical than the M/D plastic module. Consequently, this is the preferred technology recommended by the feasibility study committee.

The liquid product from the pyrolysis reactor is transferred to a hydrocracking reactor that operates at a temperature of 440-450 °C under a relatively low hydrogen pressure of 100-200 psig. The residence time is approximately one hour. Depending on the product desired, this reactor can be operated either catalytically or non-catalytically. Catalytic operation with a solid acid catalyst (HZSM-5, SiO₂-Al₂O₃, ZrO₂/WO₃, etc.) or a metal-promoted solid acid catalyst in this reactor will increase the yield of gasoline range, higher octane, product, as discussed earlier.⁽²²⁻³⁵⁾ Chlorine

levels of the product leaving this reactor should be reduced to 10-20 ppm or less. ⁽⁴¹⁾

Upgrading module: The upgrading module is fairly standard with one or two exceptions. First, since the feeds will all be hydrocarbon liquids with relatively high hydrogen contents, the hydrogen consumption of the upgrading module will be small. Depending on the exact mix of liquid feedstocks, the hydrogen pressure may also be kept fairly low. For example, if only liquid products from waste plastic are to be upgraded, they will be predominantly aliphatic, relatively light, and low in heteroatom concentration as they leave the plastic module. Thus, relatively low hydrogen pressures (200-1000 psig) should be adequate in the hydrogenation reactor. Tire pyrolysis oil is reasonably light and high in hydrogen (~12 %), but it is more aromatic than the plastic-derived oil and contains 0.5-1% N and 0.5-2% S. Consequently, higher hydrogen pressures (1000-2000 psig) are required for catalytic upgrading. If coal is substituted for tires, the resulting pyrolysis liquids will not only be high in heteroatom content, but will also be substantially heavier than the oils derived from either plastics or tires and will require hydrogen pressures of 2000 psig or higher. It is evident that hydrogen pressure and consumption in the upgrading module will depend strongly on the mix of feedstocks used and the final use of the upgraded product. Nevertheless, since all feedstocks envisioned for the demonstration plant are liquid and are fairly high in hydrogen content (10-14%), the committee felt that a single, catalytic, slurry phase, hydrogenation reactor would be adequate for the upgrading module.

The choice of catalyst will be dependent on the nature of the feed to the upgrading module and the desired properties of the upgraded product. The feeling of the committee was that for many purposes, a dispersed, nanoscale, iron-based catalyst added at a concentration of 1-2% would be adequate. The CFFS and other DOE Fossil Energy contractors have performed extensive research on iron-based catalysts for direct liquefaction. A relatively recent summary of this research is available in a special issue of Energy and Fuels ⁽⁷³⁾ containing papers from a symposium held at the American Chemical Society meeting in Denver in 1993. Normally, these catalysts are added as iron oxides or oxyhydroxides (ferrihydrites) and are converted to ultrafine iron sulfides (pyrrhotite) by reaction with H₂S during hydrotreatment. If higher hydrogenation or heteroatom removal activity is required, one option is to use nanoscale iron catalysts promoted by the addition of small concentrations (1-5% of the iron) of molybdenum. ⁽⁷³⁻⁷⁵⁾ It has been shown that the molybdate species in ultrafine, binary, ferrihydrites or iron oxides containing 1-5% Mo are primarily on the surfaces of the particles. ⁽⁷⁴⁾ Obviously, a developer might opt to use a more conventional hydrogenation catalyst, such as supported Ni-Mo, and a different type of reactor. However, this should have little effect on the capital costs and economic analysis.

Results from the DOE-sponsored research program and results from the KAB plant operations in Germany indicate that the product from the hydrogenation reactor will consist predominantly of light distillates (C₅ - C₃₀), some heavier oils (C₃₀ - C₄₀), and small amounts of IOM and inorganics (< 10% bottoms). Therefore, no recycle of heavy resid has been included in the demonstration plant. Furthermore, if only nanoscale Fe is used as the catalyst, catalyst recovery is unnecessary and the bottoms may be combusted to generate power, landfilled or used in some other way. At the KAB waste plastic liquefaction plant at Bottrop, bottoms are fed to coke ovens. However, if Mo is added to the Fe catalyst, it may be economically advantageous to add a recycle loop and/or process the

bottoms to recover the Mo.

VIII. Environmental Impact

As a first step in assessing the environmental impact of a demonstration plant, it was decided to address typical questions raised in the DOE Environmental Assessment Questionnaire. DOE requires that all DOE-sponsored programs complete this questionnaire prior to commencement of the project.

Many questions in the questionnaire deal specifically with the geographic location of the plant and can be answered only when a site has been selected. Hence, such questions have been omitted from consideration in this study. A DOE Environmental Assessment Questionnaire, completed except for site-specific questions, is attached as Appendix E to this report.

Although a waste plastic/used tire liquefaction plant will reduce the amount of solid waste in the environment, there is no credit for such action. In fact, it is necessary to address questions regarding any of waste generated by the process.

The operative word in assessing the environmental impact is “waste”. Any output streams from the plant released into the environment are considered waste. However, if a secondary user uses an output stream, it is classified as a by-product. Thus, from an environmental standpoint, it is highly preferable to sell an output stream, even at a very low price, rather than send it to a landfill. It is very desirable to reduce to a minimum any output stream that cannot be sold and must be landfilled. Thus, mitigation of environmental impact can have a strong impact on plant design and process economics.

Because a demonstration plant is proposed, the economy of scale is not favorable. Environmental questions are more critical for a small plant, since it may not be economical to treat waste streams on site. It would be beneficial to locate the plant at an industrial site where such waste treatment resources can be shared, such as a refinery, power plant, gasifier or incinerator that has enough excess capacity to handle waste streams generated by the liquefaction plant.

The three major waste stream forms are solid, liquid and gaseous. In general, the solids can be sent to landfill sites without much concern. Gaseous streams have to be treated on site due to high transportation costs. Liquid streams can be either treated onsite or transported, depending on the quantity and the treatment required.

Since the plant design is modular by nature, the envisioned waste streams are discussed on a modular basis. A complete environmental assessment requires contingency plans for unexpected accidental release of waste streams as well as startup/shutdown waste generation. Such transient waste streams are not considered in this report. Instead, the waste streams discussed are for steady state operation. The current assessment of the waste streams is considered to be qualitative, rather than quantitative, in nature.

Tire Module:

Gas: Gases generated during pyrolysis will be burned to generate process heat. The pyrolysis gas stream is expected to be less than 0.5% H₂S. To achieve zero SO_x emission, the combustion gas derived from the pyrolysis gas will have to be scrubbed.

Liquid: All pyrolysis liquid will be upgraded.

Solids: The pyrolysis residue from tires will be magnetically separated into steel wire, which can be sold as scrap steel at \$40 per ton, and carbon black. Markets for activated, upgraded, carbon black must be explored but a conservative estimate of its value is 10¢ per pound.

One problem foreseen with this module is dust generation. The pyrolysis and solids handling systems will require good seals to minimize the dust.

Waste plastics module:

Gas: During pyrolysis at 600 °C, 80-90% of the waste plastic feed will be volatilized. Essentially all of the chlorine from PVC is released as HCl. Addition of appropriate sodium or calcium compounds to the pyrolysis reactor will cause reaction of > 99% of the HCl to form harmless chlorides that are retained in the solid residue. Nevertheless, it may still be necessary to scrub the gas stream to remove any remaining HCl. It may be necessary to scrub using a neutralizing agent, such as ammonium hydroxide. The wastewater treatment plant has to handle the sludge from this operation as well as the organics. The condensed pyrolysis oil will be sent to the upgrading module. The scrubbed gas stream will contain C₁-C₄ as well as CO, CO₂ and H₂O and will be combusted for process heat or flared.

Liquid: The liquid streams will be sent to the catalytic hydrocracker and the upgrading module.

Solids: The solid residue should constitute less than 10% of the waste plastic feed. The primary constituents of the residue will be aluminum foil and other inorganics, coke or char derived from paper and other non-plastic carbonaceous material, and sodium or calcium chlorides. This residue will probably be sent to a landfill, but it may require further treatment to remove any remaining organics. As noted earlier, Al foil is recovered from the M/D reactor at the KAB liquefaction plant in Germany and sold as a byproduct. However, this will not be practical using a pyrolysis reactor.

Upgrading module:

Gas: Most of the gas from the upgrading module will be unreacted hydrogen. The economics of recovering the hydrogen from this waste stream at this scale of plant is not yet clear. However, since this gas stream will also contain reduced forms of heteroatoms (principally Cl, S, N and O), it may have to be scrubbed/neutralized before flaring/venting.

Liquid: Liquids from this module are products and will be sold.

Solids: Atmospheric and vacuum bottoms will contain all of the Fe-based once through catalyst. These bottoms might be useable as a component of asphalt. A more likely use is combustion for process heat or power. However, they will have to be characterized properly (calorific value, ash, heteroatom content, etc.) to determine if this is practical. Landfilling is the least attractive option; leaching tests on the bottoms would first have to be performed.

IX. Economic Analysis

Performing an accurate economic analysis for the demonstration plant was difficult for several reasons. First, the committee decided that a reasonable processing capacity for a first demonstration plant would be 200 tons per day of plastics and 100 tons per day of tires (approximately 10,000 tires per day). Since most previous direct liquefaction economic analyses have been done for much larger plants using coal as the feedstock, it was necessary to estimate the capital cost of several units in the plant by scaling down the cost of much larger units. Second, in some cases, equipment cost quotations from two or more manufacturers were quite different. For example, it was necessary to estimate the cost of equipment for shredding waste plastic and removing metal and other impurities from the shredded plastic. However, the equipment cost quotations received from several different vendors varied by more than an order of magnitude. Third, as the study proceeded, the committee identified several unanswered research questions related to the conceptual design of the plant. These unanswered questions have led to new research projects within the CFFS dealing with the pyrolysis of waste plastic⁽⁴¹⁾ and with the activation and upgrading of carbon black from tires^(70,71). This research has had a significant impact on plant design.

Because of these problems, the uncertainty in the economic analysis results is considered to be fairly large (, 30 %). Independent economic analyses were performed for the demonstration plant by Mahmoud El-Halwagi and Mark Shelley⁽⁷⁶⁾ of the CFFS and Auburn University and by Harvey Schindler⁽⁷⁷⁾ of Burns & Roe Services Corporation. These analyses are summarized in Appendices F and G to this report. In the current section, we have attempted to incorporate the best aspects of both of these economic analyses, incorporated information from the new research efforts noted above and included new, improved, estimates of plastic shredding and preparation costs.

The modular design of Figure 4 lends itself to economic analysis of a number of different configurations that include either two or three modules. Briefly, the three principal modules are:

- (1) Tire module – Shredding of tires to nominal 2-4 inch size, tire pyrolysis, magnetic separation of steel wire, and activation/upgrading of carbon black.
- (2) Waste plastic module – Shredding of waste plastic to 1-10 cm size, magnetic/physical cleaning, pyrolysis at approximately 600 °C with capture of chlorine as sodium or calcium chlorides, and catalytic hydrocracking of the pyrolysis liquid product.
- (3) Upgrading module - catalytic upgrading of the liquid products from modules 1 and 2 in a slurry phase reactor using a dispersed, nanoscale, iron-based catalyst and distillation of the upgraded product.

Modular design cases considered:

A variety of modular combinations were subjected to economic analysis. In the current section, the economic analysis results will be presented for the following cases:

1. Tire module + waste plastic module + upgrading module operating with 200 tons/day (t/d) of waste plastic and 100 t/d of tires. This case was selected by the committee as the base case against which other configurations were to be compared.
2. Waste plastic module + upgrading module operating with 300 t/d of plastic.
3. Tire module + upgrading module operating with 300 t/d of tires.
4. The base case (1.) with the substitution of coal for 20% of the tires.
5. Case 3. with the substitution of coal for 20% of the tires.

6. The base case (1.) with the substitution of waste oil and/or resid for 20% of the liquids entering the upgrading module.
7. The base case (1.) for a plant doubled in size or quadrupled in size.

Tipping fees:

The economic analysis results for all of the cases considered depend heavily the tipping fees received for the waste plastic and tires. In the analysis performed by Schindler (Appendix G), it was assumed that the tires were shredded elsewhere and delivered to the plant in shredded form (nominal size, 2-4 inches) at a cost of \$20/ton. This is approximately the price paid by some utility companies that burn shredded tires. The analysis by El-Hawagi and Shelley (Appendix F) considered that whole tires were accepted at the plant for a tipping fee of \$0.75 per tire or \$75 per ton and the tire shredding was performed at the plant. Tipping fees of \$0.75-1.00 per tire are typical of what is received by waste tire processors (Appendix A). A third scenario considered here is that of receiving shredded tires at the plant for free, while a fourth scenario envisions receiving a tipping fee of \$20 per ton for accepting shredded tires. The latter two scenarios were included on the basis of discussions between committee members and officials with the state departments of environmental resources (DER) in two states, West Virginia and Kentucky. In those discussions, it was indicated that the states of West Virginia and Kentucky dispose of a significant percentage of their waste tires by first shredding them and then placing them in landfills, paying ~\$20 per ton for shredding and ~\$30 per ton in landfill tipping fees. On that basis, it seemed reasonable that a plant developer might be able to establish contracts with one or several states to accept shredded tires either at no cost or for a tipping fee that was somewhat less than that charged by landfills. Thus, the tipping fees for tires in several cases considered in this analysis were set at -\$20, \$0, \$20, and \$75 per ton.

Tipping fees for placing waste plastics in landfills vary widely in the U.S., but typically are in the range from \$30-60 per ton. In the current study, the return on investment (ROI) was calculated as a function of the plastic tipping fee, from \$20-100 per ton.

Product values:

The following values were assumed for the products and byproducts of the demonstration plant.

Distillate oil - \$20 per barrel

Activated and upgraded carbon black - \$200 per ton

Steel wire - \$50 per ton

Aluminum foil - \$200 per ton

As discussed by Schindler in Appendix G, these are fairly conservative values. The effect of increasing oil prices to \$25 per barrel was also considered. This is in accord with the stated goal of the Department of Energy to develop an alternative source of oil from waste plastics, tires, and coal at a price of \$25 per barrel.⁽⁷⁸⁾ The effect of producing activated carbon of higher value, \$500/ton, was also considered for case 4, in which tires are the only plant feedstock.

Economic analysis for case 1 - 200 T/d of waste plastic + 100 T/d of tires:

Case 1 is the so-called base case illustrated by the flowsheet in Figure 4. As discussed earlier, recent research⁽⁴¹⁾ indicates that pyrolysis of the waste plastic and tires followed by hydroprocessing of the pyrolysis liquids is the best option and the flowsheet is based on this concept. However, a different technology has been developed for waste plastic in Germany (see Appendix B and reference 10).

This is illustrated by Figure 5a. In this approach, the first reaction of the plastic is a long residence time, low temperature, melting and depolymerization treatment. Since this technology has been successfully operated on a large scale (80,000 tons/year) in Germany, it is first appropriate to compare the economic analyses for the base case plant using either a pyrolysis or a melting/depolymerization (M/D) reactor in the plastic module.

A comparison of capital costs in millions of dollars (\$MM) for the two approaches is given in Table 5. A brief explanation of some of the capital costs may be useful.

Tire shredder: Quotations obtained from five vendors for a unit capable of shredding 100 tons of tires/day ranged from \$212,000 to \$471,000. The average of these quotations is given.

Tire pyrolysis reactor: Several quotations were available (Appendices F and G). Because of the desire to recover carbon black and steel wire as byproducts, an Auger-fed unit such as that described by Conrad industries⁽³⁸⁻⁴⁰⁾ may be most suitable.

Plastic shredding & preparation: Based on information obtained in Germany (Appendices B and C), the preparation of the waste plastic required to achieve the relatively uniform, granulated, feedstock that is needed for smooth operation of the M/D reactor is fairly elaborate. After shredding, several magnetic and physical cleaning steps and an agglomeration process are required. After some effort, we obtained a quotation from ERMAFA Kunststofftechnik Chemnitz GmbH & Co., one of the German companies that has been involved with the development of waste plastic preparation technology that appears to be reasonable. It includes two parallel lines, each capable of processing 100 tons/day of waste plastic, that include shredders, agglomerator units, dust removal and control systems, enclosure-housing, and control systems at a total cost of \$3.459 million.

Prior to plastic pyrolysis, on the other hand, a much simpler preparation procedure is envisioned. It includes shredding to sizes of 1-10 cm, followed by magnetic, eddy current and possibly additional cleaning steps. The quotation shown in Table 5 for the shredder units required for this type of operation (\$850,000) was obtained from Nordfab Systems, Inc., an American subsidiary of the German company (Vecoplan) that builds most of the plastic shredders used in Germany.

Plastic liquid hydrocracker: Based on results obtained in Germany (Appendix B and reference 10), the liquid leaving the M/D reactor will contain 0.1-0.2% chlorine. However, with the addition of sodium or calcium compounds to the pyrolysis reactor, the pyrolysis liquids are found to contain only about 50-200 ppm of chlorine.⁽⁴¹⁾ Consequently, the hydrocracker for the M/D liquid will require an expensive alloy such Hastelloy C, while the hydrocracker for the pyrolysis liquid can use stainless steel (see Appendix F and reference 79). This is the reason for the difference in the estimated costs for the hydrocracker units. Furthermore, it might be possible to use even cheaper steels for the pyrolysis case.

Hydrogenation reactor: On the basis of the research summarized earlier in the **Research Summary** section, the chlorine content of the liquid product entering the upgrading reactor should not exceed 10-20 ppm. Consequently, steel resistant to chlorine corrosion is not required. The estimate shown is taken from Appendix G and represents a scaled down value from an analysis performed by

Bechtel for a relatively large coal liquefaction plant.⁽⁸⁰⁾

Unit	M/D (\$MM)	Unit	Pyrolysis (\$MM)	Comments
Tire shredding	0.382	Tire shredder	0.382	Average of 5 quotations.
Tire pyrolysis	4.400	Tire pyrolysis	4.400	Average of several quotations.
Plastic shredder & preparation	3.459	Plastic shredder & preparation	0.850	Ermafa quotation - M/D; Nordfab quotation - pyrolysis.
Magnetic/eddy current units	0.081	Magnetic/eddy current units	0.081	Deng magnetic group quotation.
Plastics M/D reactor	8.000	Plastic pyrolysis reactor	7.100	Average of cost estimates from several sources.
Condenser/scrubber	0.330	Condenser/scrubber	0.330	Appendix G
Plastic liquid hydrocracker	10.905	Plastic liquid hydrocracker	5.556	More corrosion resistant alloy for M/D case.
Carbon black activation	1.360	Carbon black activation	1.360	Based on recent research and literature data.
Hydrogenation reactor	4.703	Hydrogenation reactor	4.703	Scaled down from larger unit - Cl resistant alloy not necessary.
Hydrogen separation	0.889	Hydrogen separation	0.889	Average of values given in Appendices F and G.
Product fractionation	0.717	Product fractionation	0.717	Average of values given in Appendices F and G.
General offsites /land	10.568	General offsites /land	7.910	30% of above costs.
Total capital costs	45.794	Subtotal	34.278	
Contingency (20%)	9.159	Contingency (20%)	6.856	20 % of total capital costs.
Total Capital Investment	54.953	Total Capital Investment	41.134	

Table 5. Capital costs estimates for the base case plant (200 t/d of plastic and 100 t/d of tires) using either a melting/depolymerization (M/D) reactor or a pyrolysis reactor for the plastic conversion from solid to liquid.

General offsites: General offsites includes the costs of land, buildings, plumbing and wiring, control systems and other items.

The estimated annual operating costs for the base case plant using either the M/D or the pyrolysis plastic module are given in Table 6. To a good approximation, these costs are estimated to be the same with the exception of maintenance costs. Maintenance costs are set at 5% of capital costs. ⁽⁷⁹⁾

Cost Item	M/D (\$MM)	Pyrolysis (\$MM)	Comments
Shredding cost	0.810	0.810	Shelley & El-Hawagi estimate - \$8.18/ton.
Maintenance	2.290	1.714	5% of total capital costs.
Labor	2.330	2.330	Assumes 80 employees; 60@\$12/hr, 20@\$20/hr.
Utilities	0.893	0.893	Average of values given in Appendices F & G.
Purchased hydrogen	0.774	0.774	Average of values given in Appendices F & G.
Catalysts	0.600	0.600	\$300K/yr for both solid acid and hydrogenation catalysts.
Lime	0.139	0.139	Assumes \$15/ton for 28 T/d limestone
Other chemicals	0.083	0.083	Average of values given in Appendices F & G (Amoco-Bechtel study).
Solid waste disposal	0.264	0.264	\$50/ton for landfilling.
Wastewater treatment	0.009	0.009	Appendix G
Total	8.192	7.616	

Table 6. Operating cost estimates for the base case plant (200 t/d of plastic and 100 t/d of tires) using a melting/depolymerization (M/D) reactor (left) or a pyrolysis reactor for the plastic conversion from solid to liquid.

Table 7 gives an example of the results for total revenues, profits and returns on investment (ROI) for the base case plant using either the M/D or the pyrolysis plastic module. On the basis of the experimental results for oil yields from plastic and tires, it is estimated that approximately five barrels of oil will be produced per ton of plastic and 2.5 barrels per ton of tires, or a total of 1250 barrels per day for the base case plant. The average of several investigators' results for tire pyrolysis^(41,55,56) for recoverable byproducts is approximately 12% steel wire and 28% carbon black. This assumes that the ash content of the carbon black has been reduced to about 1-2%. On the basis of results for carbon black activation,⁽⁶⁹⁻⁷¹⁾ about 40% of the carbon will be oxidized away in the activation process. Therefore, the plant should produce 12 tons/day of steel and 17 tons/day of activated carbon. For the M/D case, it is assumed that the aluminum foil is recovered from the plastic as a byproduct and that its concentration is 0.75 wt.%. Finally, it is assumed that the plant operates 330 days per year.

The returns on investment (ROI) for the base case plant (200 t/d of waste plastic, 100 t/d of tires) using either an M/D reactor or a pyrolysis reactor in the plastic module are compared in Figure 6. In most of the country, landfill tipping fees are \$30-60/ton. Consequently, in Figure 6, the ROIs are shown for plastic tipping fees of either \$30 or \$60/ton for waste plastic and for the four different tire

tipping fee scenarios discussed earlier. The results clearly show that the use of a pyrolysis reactor

Products	Value (\$/bbl or ton)	Quantity (bbl or tons/yr)	Revenue (\$MM/yr)
Oil	20.000	412500.000	8.250
Carbon	200.000	5610.000	1.122
Steel	50.000	3960.000	0.198
Aluminum	200.000	495.000	0.099
Plastic tipping fee	30.000	66000.000	1.980
Tire tipping fee	75.000	33000.000	2.475
Total revenue			14.124
Profit - M/D			5.932
ROI (%), M/D			10.795%
Profit - pyrolysis			6.409*
ROI (%) - pyrolysis			15.581%

*Does not include revenue from aluminum foil.

Table 7. Typical calculation of revenues, profits and ROIs for the base case plant using either the M/D or the pyrolysis plastic module.

in the plastic module has a significant economic advantage over the use of the M/D reactor, despite a small loss in revenue due to not recovering aluminum foil. Consequently, the pyrolysis plastic module is the only one considered in the remainder of this section. Additionally, it is also seen in Figure 6 that the economic gain from receiving whole tires at the plant and shredding them there easily offsets the extra capital and operating costs associated with the shredding operation.

Figure 7 shows the ROI for the base case plant using the pyrolysis plastic module as a function of plastic tipping fee for several oil prices. The tipping fee for tires is held constant at \$75/ton. It is seen that ROIs of 20-30% are not unreasonable for the base case plant.

Economic analysis for case 2 - 300 tons/day of waste plastic:

Since some developers may be interested only in waste plastic, it is of interest to consider a plant consisting only of the plastic and upgrading modules. The simplified flow sheet is shown in Figure 8. It is assumed that the total amount of material processed per day remains the same, 300 tons. It is further assumed that labor and most other operating costs remain the same. Maintenance is again taken as 5% of total capital costs. These are fairly conservative assumptions since, with fewer operations, operating costs would be expected to decrease, even with the same total throughput of material. To estimate the capital costs of the larger units required to process 300 tons per day of plastic as compared to 200 tons per day for the base case, the scaling law,

$$\text{Cost} \propto (\text{Size})^{0.7} \tag{1}$$

has been used. Again, this is fairly conservative.

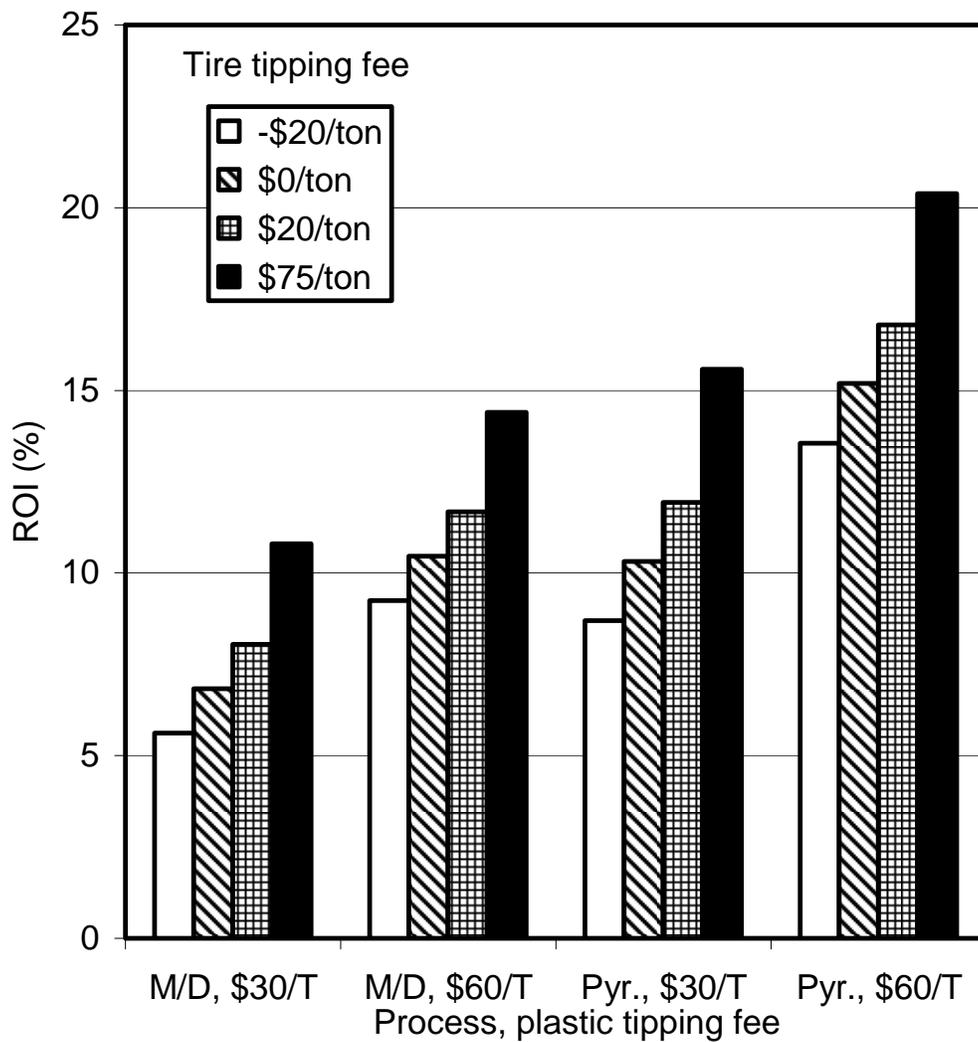


Figure 6. Comparison of ROI for plants using either an M/D or a pyrolysis reactor to convert waste plastic to liquid as a function of plastic and tire tipping fees.

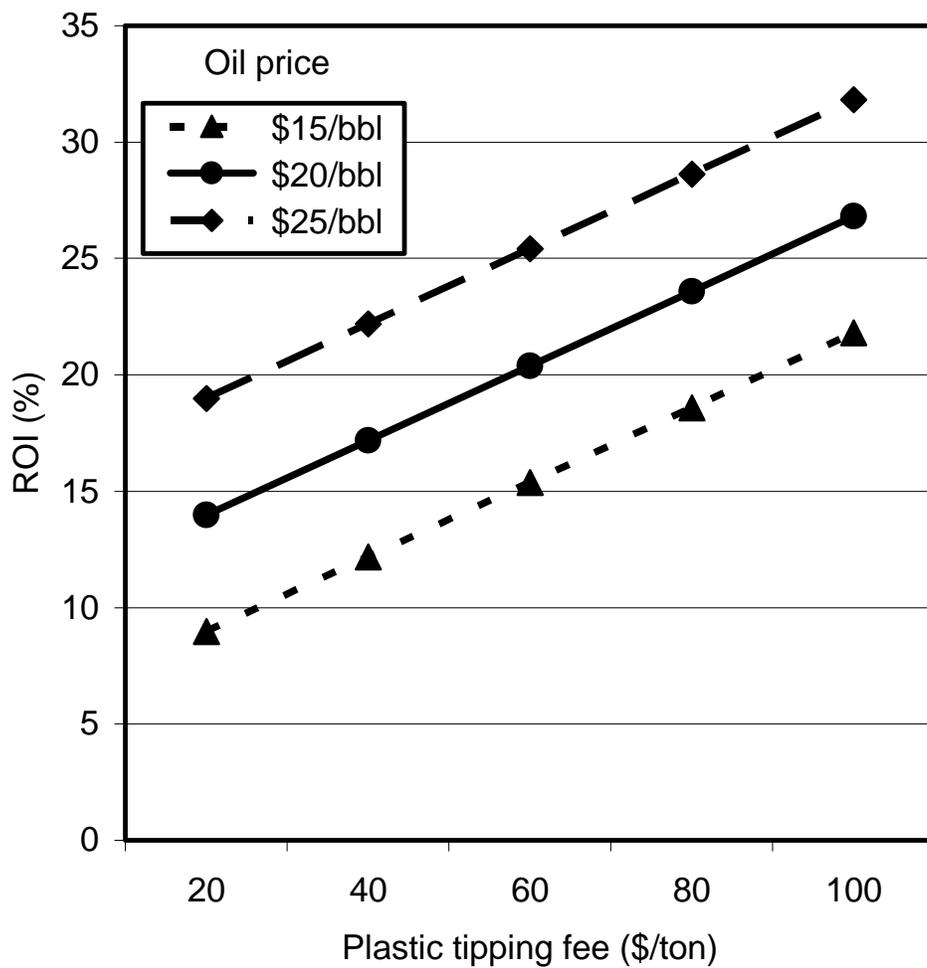


Figure 7. ROI vs. plastic tipping fee for several oil prices. Base case, tire tipping fee - \$75/ton. Pyrolysis reactor to convert plastic to liquid.

The resulting capital costs and operating costs for the 300 t/d plastic plant are given in Table 8. It is seen that they are fairly close to the costs for the base case plant. The predicted ROI as a function of plastic tipping fee is shown in Figure 9 for several oil prices. With oil priced at \$20 per barrel, the predicted ROI ranges from 10 to 30% as the tipping fee increases from \$20 to \$100 per ton. An increase in the price of oil by \$5/barrel or in the waste plastic tipping fee by \$30/ton increases the ROI by about 5%. It seems unjustified to consider any higher oil prices or landfill tipping fees than those shown in Figures 7 and 9 at this time.

Equipment Unit	Capital cost (\$MM)	Cost Item	Operating cost (\$MM/yr)
Plastics shredder	1.129	Shredding cost	0.810
Magnetic/eddy current separators	0.108	Maintenance	1.659
Plastic pyrolysis	9.429	Labor	2.330
Condenser/scrubber	0.438	Utilities	0.893
Plastic liquid hydrocracker	7.378	Purchased hydrogen	0.774
Hydrogenation reactor	5.343	Catalysts	0.600
Hydrogen separation	0.889	Lime	0.139
Product fractionation	0.815	Other chemicals	0.083
General offsites/land	7.659	Solid waste disposal	0.396
Total capital cost	33.188	Wastewater treatment	0.009
Contingency (20%)	6.638	Total operating cost	7.693
Total Capital Investment	39.825		

Table 8. Capital costs and annual operating costs for a plant processing 300 tons/ day of waste plastic.

Economic analysis for case 3: 300 tons/day of waste tires

Anticipating that some developers may only be interested in processing waste tires, it is of interest to consider a plant consisting of the tire module and the upgrading module which processes 300 tons of tires (30,000 tires) per day. The flow sheet is shown in Figure 10. Using the capital and operating costs from Table 5 and 6 and the scaling relation of Equation 1, the cost estimates given in Table 9 are obtained.

The ROI has been calculated as a function of tire tipping fee, oil price and activated carbon price. Two values are illustrated for each of these controlling factors in Figure 11. One option for tire acquisition is to purchase tires in shredded form. This reduces operating and capital costs somewhat (\$0.81 million – capital, \$1 million - operating). However, this is easily offset by the purchase price of the shredded tires (\$1.98 million) and the loss of tipping fees that would be earned by accepting whole tires and shredding them at the plant (\$7.4 million). Shredding tires at the plant is clearly advantageous, producing nearly a 30% increase in the ROIs. With regard to oil price, it is again seen that increasing the price from \$20 to \$25 per barrel produces approximately a 5% increase in

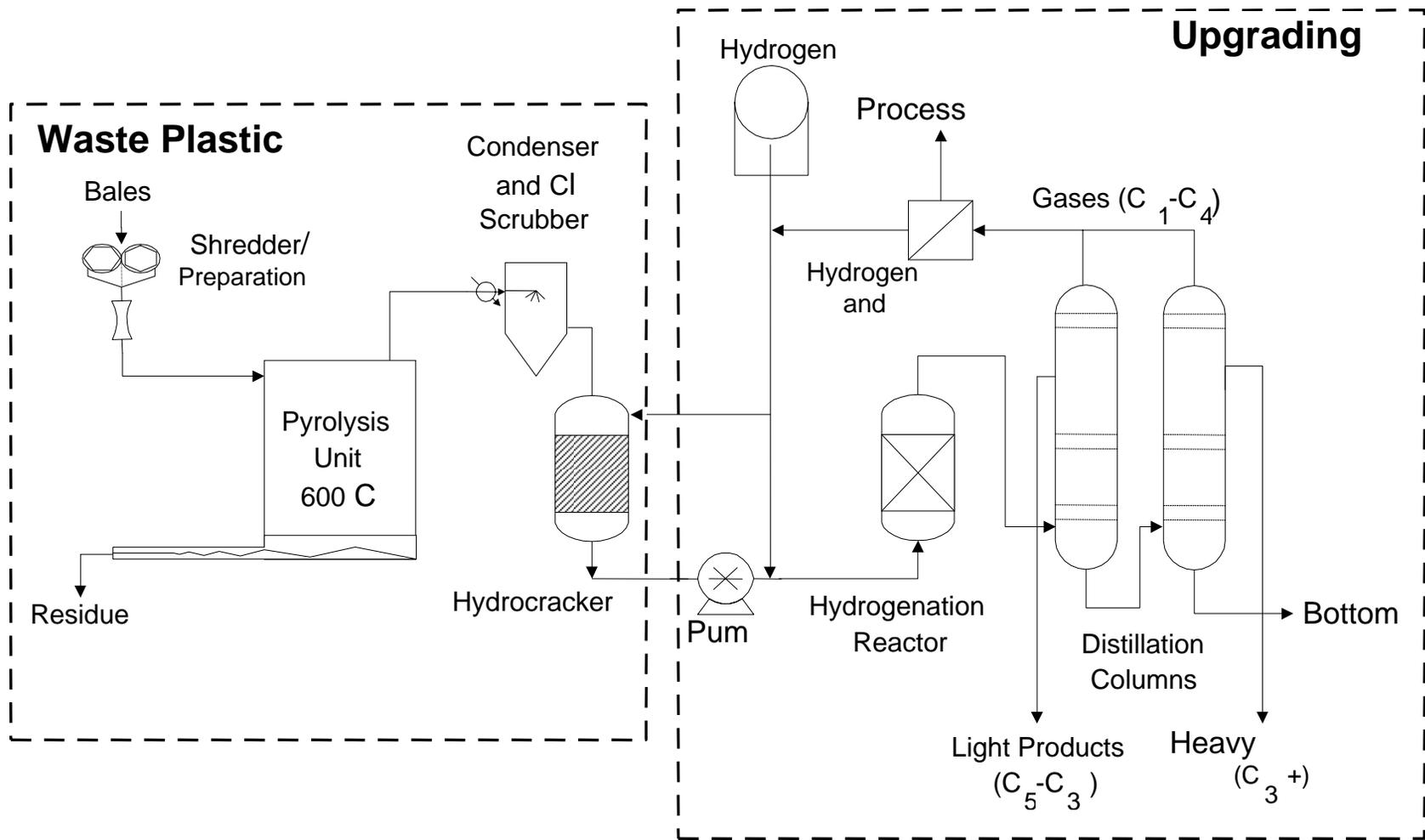


Figure 8. Conceptual design for a demonstration plant for liquefaction of waste

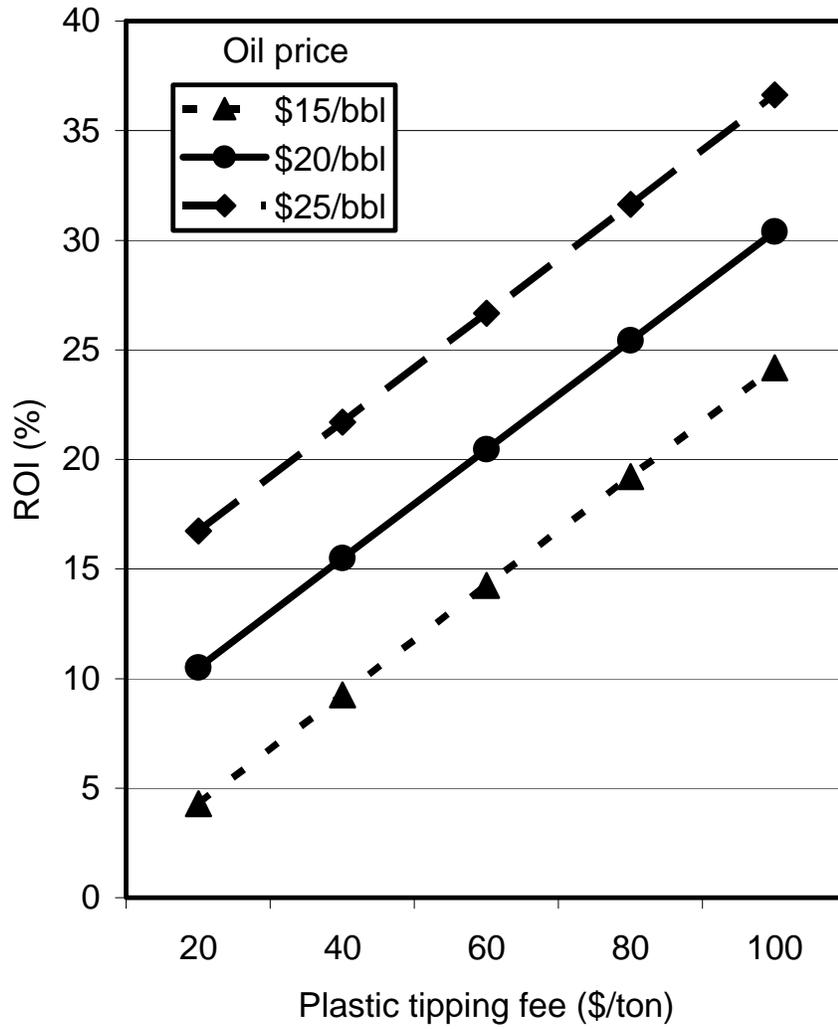


Figure 9. ROI vs. plastic tipping fee for a plant converting 300 tons/day of waste plastic to oil.

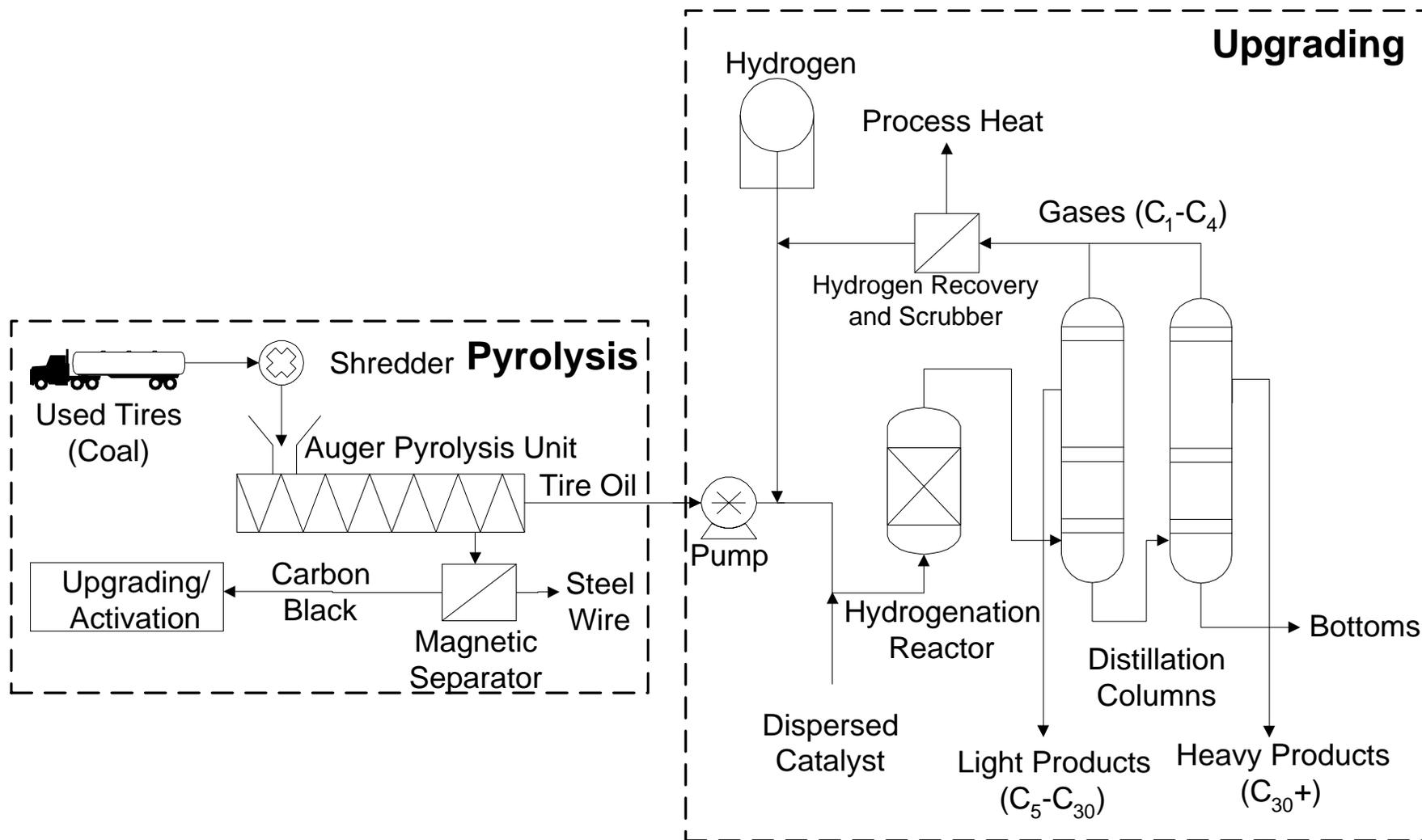


Figure 10. Conceptual design for a demonstration plant for liquefaction of tires with recovery of carbon and steel wire.

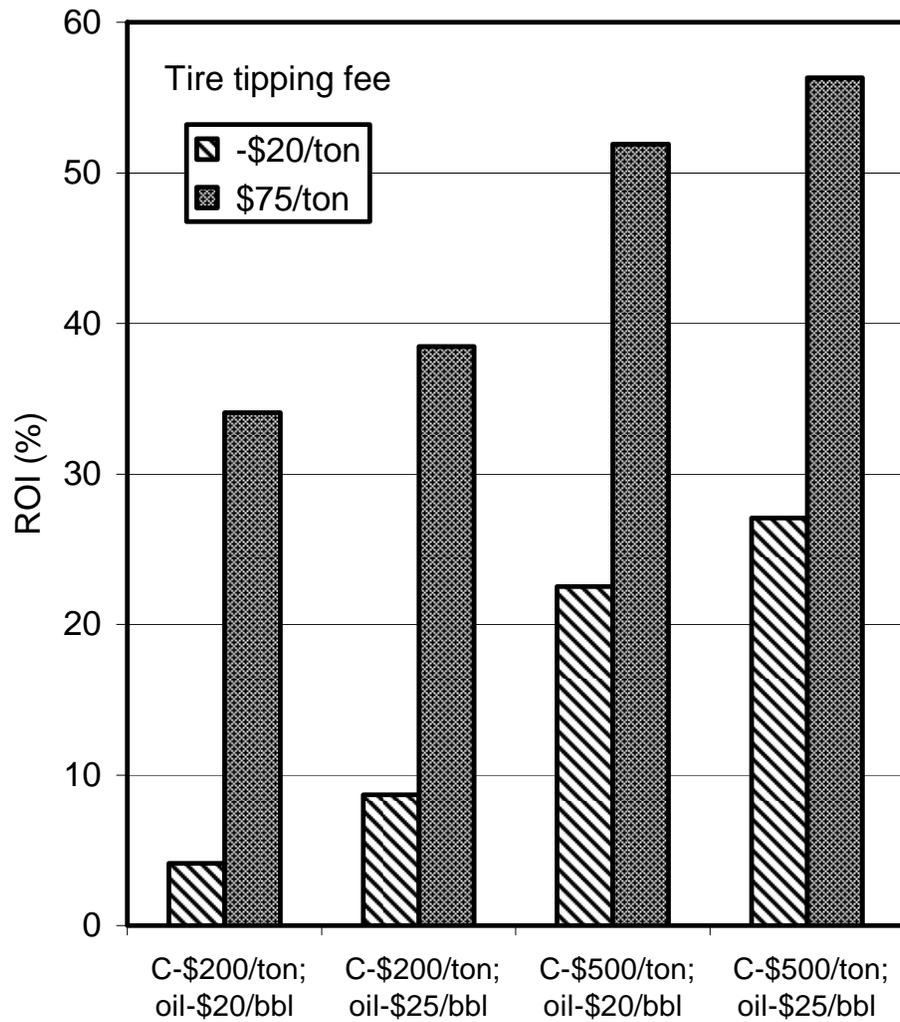


Figure 11. ROI for a plant processing 300 tons/day of tires as a function of the price of carbon and oil. Results are shown for two tipping fees.

Equipment Unit	Capital cost (\$MM)	Cost Item	Operating cost (\$MM/yr)
Tire shredder	0.826	Shredding cost	0.810
Tire pyrolysis	9.494	Maintenance	1.166
Carbon black separation/activation	2.934	Labor	2.330
Hydrogenation reactor	3.287	Utilities	0.893
Hydrogen separation	0.889	Purchased hydrogen	0.774
Product fractionation	0.501	Catalysts	0.300
General offsites/land	5.379	Lime	0.139
Total capital costs	23.310	Other chemicals	0.083
Contingency (20%)	4.662	Solid waste disposal	0.264
Total Capital Investment	27.972	Wastewater treatment	0.009
		Total operating cost	6.768

Table 9. Capital costs and annual operating costs for a plant processing 300 tons/ day of waste tires (30,000 tires per day or 9.9 million tires per year).

the ROI. Finally, it is seen that increasing the value of the carbon product from a conservative price of \$200 per ton (10¢ per pound) to a more optimistic price of \$500 per ton (25¢ per pound) increases the ROI by nearly 20%. In view of the research results discussed earlier, ⁽⁶⁹⁻⁷¹⁾ carbon priced at \$500 per ton does not seem unrealistic.

Cases 4-6 – Replacement of polymer feedstocks by coal or waste oil/resid

It is probable that there will be times when the supply of waste plastic or tires is insufficient to maintain operation of the plant at the desired throughput. As previously discussed in the **Research Summary** section, coal can be substituted for tires feeding the pyrolysis unit in the tire module, while waste oil or resid can replace the liquid product from either the plastic or tire module. It is therefore of interest to consider the effects of such replacements on the economics of the operation. Here, we consider replacing 20% of the tires by bituminous coal or 20 % of the liquid product from the plastic module by waste oil or resid.

Effect of replacing tires by coal For the base case plant (200 t/d of plastic, 100 t/d of tires), a 20% replacement of tires by coal is equivalent to feeding the pyrolysis unit in the tire module with 80 tons per day of tires and 20 tons per day of coal. For the plant processing only tires, it is equivalent to feeding 240 tons per day of tires and 60 tons per day of coal. The effects of such replacement on the ROI are illustrated in Figure 12. For all cases shown, the tipping fee for tires is assumed to be \$75/ton, while the tipping fee for waste plastic in the base case is taken as \$60/ton. The following assumptions are made in deriving the ROI: (1) coal is purchased for \$25 per ton; (2) on pyrolysis, coal yields 20% liquid, 10% gas, and 70% char; and (3) the char can be sold as fuel for \$15 per ton. Not surprisingly, the decrease in the ROI is significantly greater for the tires only plant than for the base case plant. With the carbon product valued at \$500/ton, the ROI decreases from over 50% to

under 40%. Nevertheless, for all of the cases shown, the ROIs with coal replacing 20% of the tires are still quite reasonable.

Effect of replacing the liquid entering the upgrading module with waste oil or resid If the demonstration plant is associated with a refinery, the most logical replacements for waste polymers would be waste oil or petroleum resid. If it is assumed that 20% of the liquid entering the upgrading module is replaced by waste oil/resid, and if the waste oil/resid is provided from refinery operations at no charge, the only loss of income will be lost tipping fees. The resulting loss in ROI is shown for the base case plant as a function of both tire and plastic tipping fee in Figure 13.

Case 7 – Effect of increasing the size of the base case plant

Although a plant size of 300 tons per day is reasonable for a first demonstration plant, it is appropriate to consider the effect of plant size on economics. Assuming that a demonstration plant operates successfully and profitably, it would seem logical to develop larger plants for more densely populated areas. Figure 14 shows the effect on the ROI of increasing the plant size by a factor of 2 or a factor of 4. In calculating the ROI for larger plants, a simple approximation is used. It is assumed that plant capital costs and operating costs increase with size by a 0.7 power law (Equation 1) and that revenue increases linearly with size. The resulting formula is

$$ROI_2 = ROI_1 \{ [(S_2/S_1) / (S_2/S_1)^{0.7}] R_1 - OC_1 \} / (R_1 - OC_1) \quad (2)$$

where S_1 and S_2 are plant sizes, ROI_1 and ROI_2 are the returns on investment, and R_1 and OC_1 are the annual revenue and operating cost for plant size S_1 .

The results obtained from Equation 2 for the base case, using the average capital and operating costs in Tables 5 and 6 and assuming conservative product values (\$20/barrel - oil, \$200/ton - carbon, and \$50/ton - steel) and tipping fees (tires - \$75 per ton, plastic - \$30 or \$60 per ton) are shown in Figure 14. The ROIs for the larger plants are attractive, ranging from 25 to 40%, depending on tipping fees.

X. Conclusions and Summary

A feasibility study has been conducted for a demonstration plant for the liquefaction of waste plastic and tires and the coprocessing of coal with these waste polymers. The principal results of the study are briefly summarized below.

Potential resource: Only about 5% of all waste plastic and 15% of the used tires produced in the U.S. are currently recycled. The total potential oil resource available from these materials and other petroleum-derived wastes is approximately 150 million barrels per year. Valuable byproducts that could be recovered from the tires include over 800,000 tons per year (t/y) of carbon black and nearly 300,000 t/y of steel. The value of this currently wasted resource is over \$3 billion per year.

German feedstock recycling industry: The current report and two of its appendices contains a fairly complete report on the German waste plastic feedstock recycling industry, which is the currently the most extensive in the world. The Duales System Deutschland (DSD) and their contractors are currently supervising the recycling of approximately 300,000 tons of waste plastic per year into oil, olefins, synthesis gas, and reducing gases for use in the production of steel in blast furnaces. The

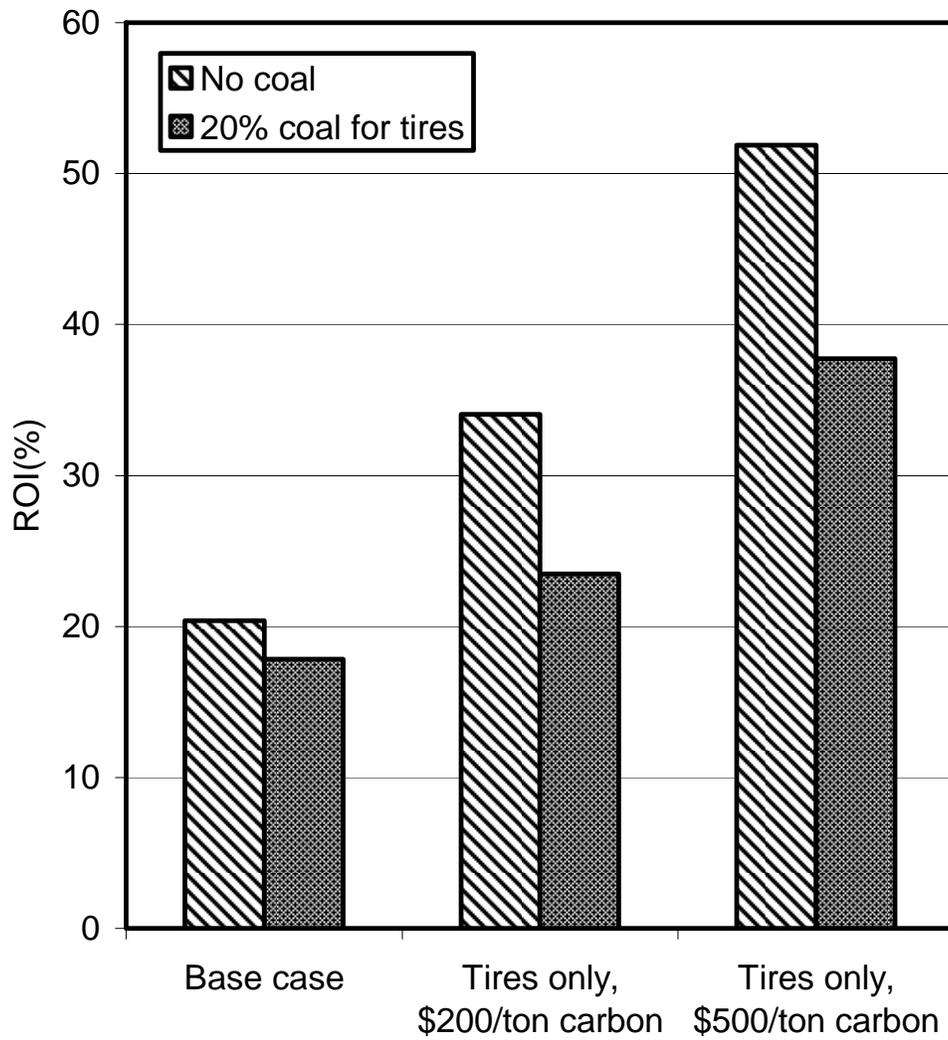


Figure 12. Effect of replacing 20% of the tires by coal for the base case plant and for a plant processing only tires.

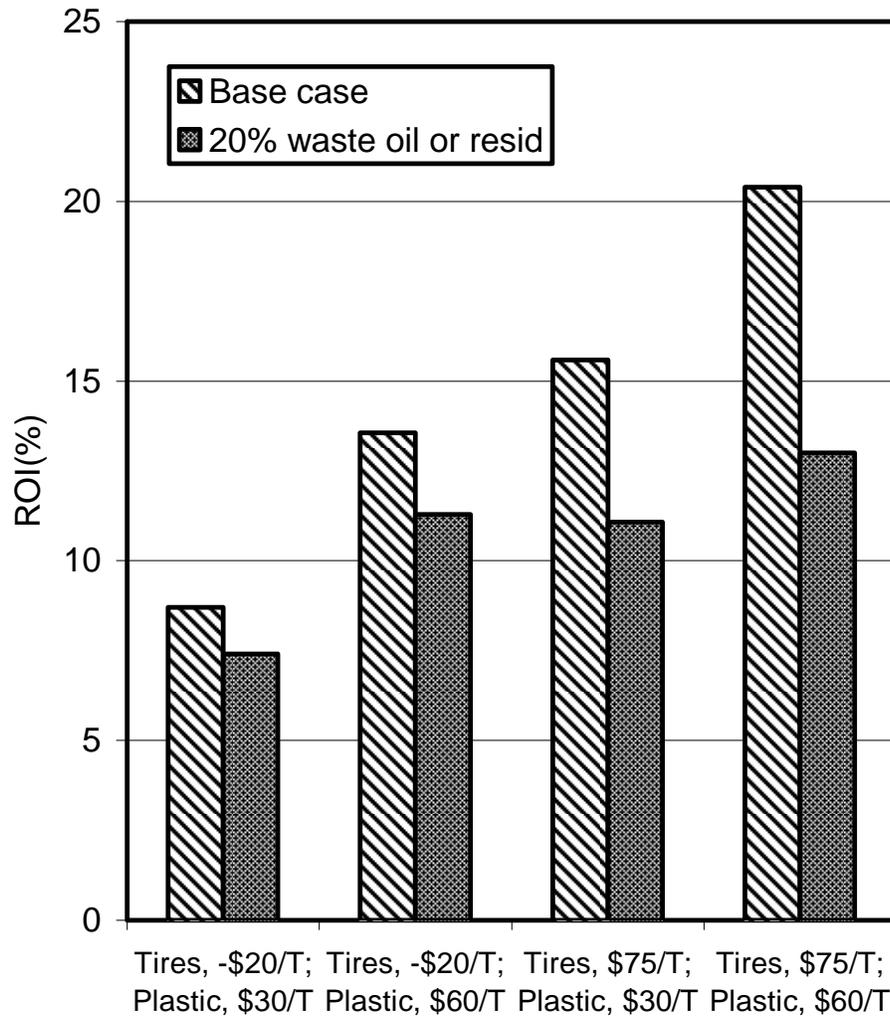


Figure 13. Effect on ROIs of replacing 20% of liquids from plastic and tires by waste oil or petroleum resid. Tire and plastic tipping fees are indicated.

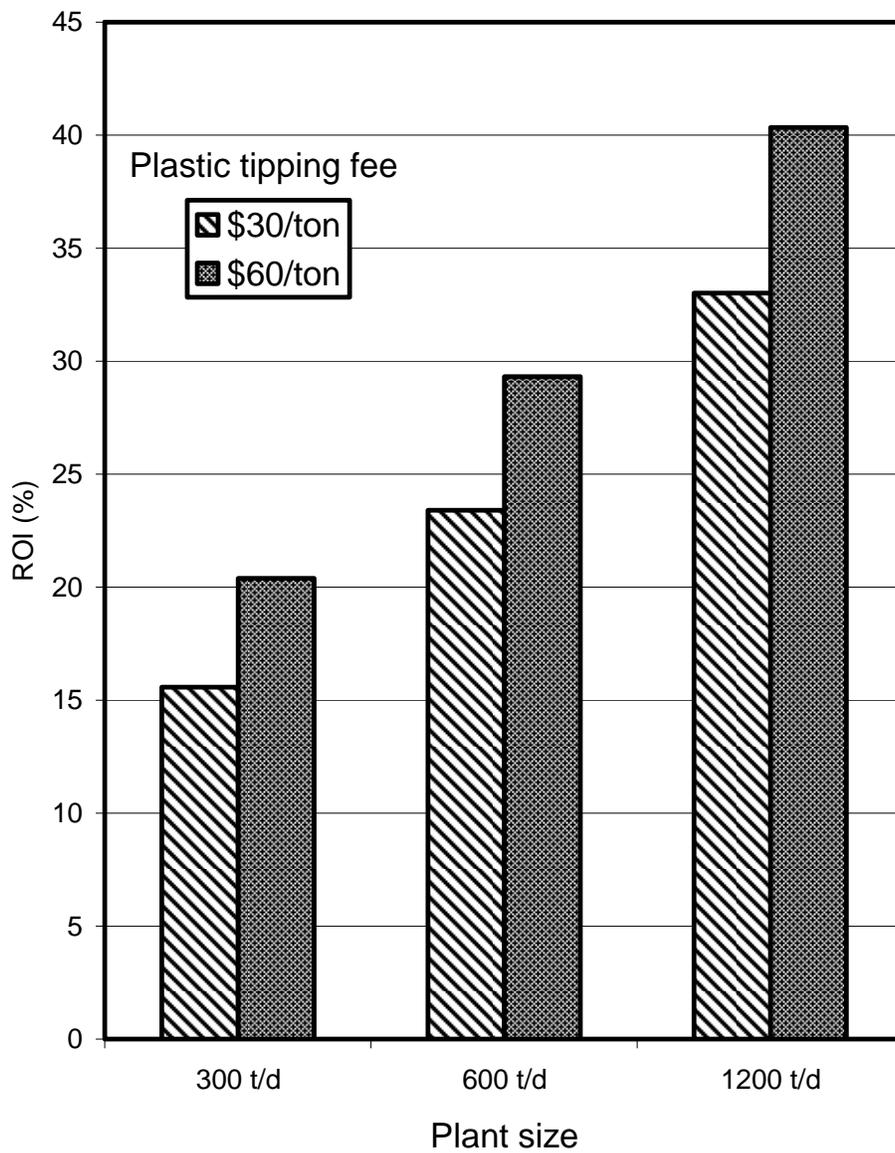


Figure 14. Effect of plant size on ROI for the base case with pyrolysis reactor to convert plastic from solid to liquid.

processing plant closest to the technology discussed in the current report is the liquefaction plant of Kohleöl-Anlage Bottrop, GmbH (KAB), which is currently liquefying 80,000 tons of DSD waste plastic feedstock per year.

Research: The status of the research program on liquefaction and coprocessing of waste polymers sponsored by the DOE is briefly summarized. Emphasis is placed on the results that are considered most pertinent for demonstration plant development.

Plant design: A modular design was chosen for the demonstration plant. The three principal modules for the base design, illustrated in Figure 4, are as follows:

Tire module – Tires are shredded and pyrolysed at 600-700 °C and the pyrolysis oil is transferred to the upgrading module. The pyrolysis residue is subjected to magnetic separation to remove steel wire and the remaining carbon black is activated by partial oxidation and upgraded by ash removal.

Waste plastic module – Third bale waste plastic is shredded and subjected to magnetic and physical cleaning processes. The shredded plastic is then pyrolysed at approximately 600 °C yielding a heavy oil that is scrubbed to remove HCl, condensed and subjected to catalytic hydrocracking. The resulting liquid is transferred to the upgrading module.

Upgrading module - Catalytic upgrading of the liquid products from modules 1 and 2 occurs in a slurry phase hydrogenation reactor using a dispersed, nanoscale, iron-based catalyst and the product is subjected to distillation. Other types of hydrogenation reactor and catalysts could be used, if desired.

A modular approach was adopted to allow potential developers to choose the modules that best suit their needs.

Economic analysis: A summary of some typical economic analysis results for various plant development scenarios (column 1) is presented in Table 10. For reasons previously discussed, the uncertainty in the results is considered to be fairly large ($\pm 30\%$). Nevertheless, they should provide reasonable guidelines to potential developers of a demonstration plant. The estimated capital cost for each scenario is given in column 2 and the predicted returns on investment (ROI) are given in columns 3-6 for: oil priced at \$20 and \$25 per barrel; plastic tipping fees of \$30 or \$60 per ton; and tires purchased in shredded form for \$20 per ton or accepted as whole tires with a tipping fee of \$75 per ton (\$0.75/tire).

The ROI results summarized in Table 10 and Figures 6-14 are very encouraging. For the base case (200 t/d of waste plastic, 100 t/d of tires), the predicted ROI with oil priced at \$20 per barrel is 9-20%. Not surprisingly, replacement of 20% of the tires by coal, or 20% of the liquids from waste polymers by waste oil or resid, lowers the ROIs. However, the loss of ROI is not catastrophic, but is typically several percent. For a plant processing 300 t/d of waste plastic alone, the ROI range is similar to the base case plant. However, the ROI for a plant processing 300 t/d of tires alone could exceed 50% with a carbon product priced at \$500 per ton. For all cases, an increase of \$5/barrel in the price of oil increases the ROIs by approximately 5%. Finally, it is seen that doubling the size of the base case plant increases the ROI by about 10%, while quadrupling the size causes a 20% increase in ROI.

		Tipping fees /prices - \$/ton or barrel				
		Plastic tipping fee ←	30	30	60	60
		Tire tipping fee (+) or price (-) ←	-20	75	75	75
		Oil price ←	20	20	20	25
Type of plant	Capital cost (\$ million)	ROI (%)	ROI (%)	ROI (%)	ROI (%)	
Base case: 200 t/d of plastic, 100 t/d of tires	41.1	8.7	15.6	20.4	25.4	
Base case with 20% of tires replaced by coal	41.1	7.7	13.0	17.8	---	
Base case with 20% of liquid replaced by waste oil or resid	41.1	7.4	11.1	13.0	---	
300 t/d of plastic	39.8	13.0	13.0	20.5	26.7	
300 t/d of tires - carbon @ \$200/ton	28.0	4.1	34.1	34.1	38.5	
300 t/d of tires - carbon @ \$500/ton	28.0	22.5	51.9	51.9	56.3	
Base case - 600 t/d (400-plastic, 200-tires)	66.8	---	23.4	29.3	---	
Base case - 1200 t/d (800-plastic, 400-tires)	108.6	---	33.0	40.3	---	

Table 10. Summary of estimated capital costs and ROIs for various demonstration plant scenarios.

XI. Future Program

This feasibility study indicates that a new industry can be developed to convert waste plastic and tires into valuable hydrocarbon fuels and byproducts. *It is considered significant that the economic analysis predicts, for the first time, that a direct liquefaction process can be profitable at current oil prices, even at the demonstration plant stage.* At current tipping fees for waste plastics and tires, returns on investment of 10-20% are possible for a 300 ton per day plant. With reasonable increases in tipping fees, product value and plant size, ROIs in the 30-50% range should be achievable. These ROIs decrease by 1-10% if 20% of the plastic and tires are replaced by coal or waste oil and resid.

Since waste plastic and tires constitute only about 12-14% by weight of all the waste materials that are landfilled, it is logical to consider similar feedstock recycling for other wastes, such as paper, yard wastes, wood wastes, biomass, and automobile shredder residue (ASR), which constitute 50-60% of landfill mass. Ideally, it would be advantageous to incorporate the conversion of these

organic waste materials with the conversion of coal, possibly within the setting of an integrated gasification combined-cycle (IGCC) power plant. Pyrolysis, hydroprocessing, gasification, and synthesis gas reaction could then be integrated to achieve the most efficient conversion of different types of waste materials into valuable hydrocarbon products. In addition to broadening the range of processes, the range of products should also be expanded to include higher value oil products, value-added chemicals, and hydrogen.

If the broader program and the industry envisioned are to become a reality, industry, government (federal, state and municipal), the academic community and environmental groups must all play a role. A brief discussion of the contributions that these segments of society can make is given below.

Government

Congress: Research funding in this area should be increased in order to mount a broader research program dealing with a wider range of waste materials. To demonstrate the viability of the program, it is important that a demonstration plant be built soon. Congress can give industry incentive for building a first demonstration plant by providing part of the capital investment and/or by providing favorable tax treatment for profits generated from the plant.

Department of Energy: DOE Fossil Energy (FE) should continue to manage and coordinate the research program. Certain components of the research should be carried out at FETC and other DOE laboratories where special capabilities exist that are not available elsewhere. DOE FE should conduct workshops with potential stakeholders in industry, other branches of the federal government and state and local government. DOE should try to establish an agreement with the Environmental Protection Agency that conversion of waste materials into oil or other hydrocarbon products is recycling. This has been accepted in Germany and other parts of Europe and in Japan. It is also important to agree not to set unrealistic quotas on the amount of plastic that must be mechanically recycled. This has been a problem in the German program.

State and local government: The siting of the initial demonstration plant should be in a state or city where prior agreements have been reached regarding contracts to deliver the required amounts of waste plastics and tires to the plant at profitable tipping fees. It will also be important to have the support and participation of local waste management companies. Once a site has been selected, state and local government will play an important role in education of the community regarding the new recycling technology.

Environmental Groups

Environmental groups should be involved in the discussions early and throughout the development of the plant. This should include representatives of the EPA, state and municipal environmental agencies and private organizations.

Academic Community

The primary role of the academic community will be to conduct the basic research required, both on remaining problems related to the proposed demonstration plant and for the broader waste conversion program envisioned. Additionally, they should participate in DOE stakeholder workshops and play a significant role in community education. The latter role will be very

important, since polls seem to indicate that the public has more confidence in the academic community than they do in either industry or government.

Industry

Ultimately, the major role of industry is plant construction and operation. However, industry should play a role in identifying the feedstocks, conversion processes and products that make the most economic sense. This will help to focus the research on products and processes for which there is a market and real potential for industrial development.

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Dr. Rolf Holighaus, Mr. Fritz Wentzel, Dr. Christian Hecka, and Dr. Klaus Nieman of Kohleöl-Anlage Bottrop (KAB) hosted two highly informative visits by committee members to their waste plastic liquefaction plant in Bottrop, Germany. Additionally, Dr. Holighaus made an excellent presentation at the annual CFFS Technical Meeting in 1996 and he and Mr. Wentzel made two trips to the U.S. for further discussions.

Mr. Bernd Strobel, Dr. Karl Van Heek and Dr. Wolfgang Wanzl of the DMT Institute for Cokemaking and Fuel Chemistry in Essen, Germany provided several CFFS scientists with tours of their laboratories and summaries of their research program on waste polymer liquefaction and pyrolysis. Mr. Strobel and Dr. Wentzel presented excellent summaries of their research at the annual CFFS Technical Meeting in 1995.

Mr. Mickey Mills, Director of the Bluegrass Regional Recycling Center (BRRC) in Lexington, KY, has provided useful information and samples to the CFFS for some time. For the current study, he conducted the survey of waste availability that is included in this report as Appendix D.

Dr. Brigitta Huckestein conducted a tour of the BASF pilot plant for conversion of waste plastics to hydrocarbon products in Ludwigshafen, Germany for several committee members.

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