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Catalytic Pyrolysis Of Plastic Wastes — Towards An Economically Viable Process

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Catalytic Pyrolysis Of Plastic Wastes — Towards An Economically Viable Process

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Abstract: The ultimate goal of our project is an economically viable pyrolysis process to recover useful fuels and/or chemicals from plastics-containing wastes. This paper reports the effects of various promoted and unpromoted binary oxide catalysts on yields and compositions of liquid organic products, as measured in a small laboratory pyrolysis reactor. On the basis of these results, a commercial-scale catalytic pyrolysis reactor was simulated by the Aspen software and rough costs were estimated. The results suggest that such a process has potential economic viability.

1 Background

The ultimate goal of this project is the design, construction, and operation of an economically viable process for the simultaneous disposal and conversion to useful products of mixed plastic waste.

The use of plastics in consumer products is steadily increasing. Because discarded automobiles, appliances, electronic equipment, etc., are often shredded for recovery of metals, a large, plastic-rich waste stream is left to be landfilled at costs often as high as $100/ton (Schmitt 1990, Tabery 1990). Other significant sources of mixed plastics, such as used tires, segregated household waste, and old carpeting, are also usually landfilled.

It would be useful to process this enormous stream of wastes to produce materials that could be sold at a profit. Attempts to separate, clean, and resell such valuable plastic materials as ABS are commendable and when this is possible, plastics recycling is a good alternative to landfilling (Karvelas et al. 1996, Jody et al. 1996). Unfortunately, the components of most plastic waste streams are too intimately mixed and contain too many low-value materials for recycling to be profitable. Other methods of treatment must be found. The most obvious possibility is

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DISCLAIMER

pyrolysis: the heating of the waste stream in the absence of air. Along with many others, we have chosen to study this possibility.

2 Objective

The reason for studying the pyrolysis of waste to recycle valuable plastic materials is the belief that a commercial-scale pyrolysis process can be profitable. Therefore, our approach has been guided by the major factors affecting profitability: construction and operating costs of the processing plant and yield[2] and value of the pyrolysis products. Work towards reducing construction and operating costs is ongoing, and early results have been reported (Brockmeier and McIntosh 1994). Effort towards improving the yield and value of pyrolysis products is also under way (Arzoumanidis et al. 1995), and this paper summarizes some recent results. We have found that catalysts have a significant effect on yield and value; therefore, catalysis will be the major topic covered in this paper.

3 Procedure

A potentially economic process must receive a large, constant flow of mixed plastic waste and must minimize the expense of handling. Therefore, we assume the flow of waste will go into the process as received, without segregation or significant pretreatment. Thus, the material fed to the process will be variable in the type and relative amounts of plastics. One reasonable way to proceed would be to study a wide range of plastics compositions in combination with a few different catalysts. However, since little is known concerning which catalysts might be effective in such applications, we have chosen instead to study a fixed composition of simulated waste in combination with a broad range of possible catalysts. In this way, we will more quickly survey a broad range of catalysts. We then hope to generalize the observed effects and thereby minimize the testing required to find catalysts effective over a range of waste compositions.

Accordingly, for all tests, we have fixed our simulated waste feed as shown in Table 3.1. The values in Table 3.1 represent the average composition of the plastic-rich waste stream recovered from an automobile shredding operation.

Tests were conducted by mixing the simulated waste with powdered

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[2] The yield of a given product of pyrolysis is the weight percent, relative to the starting material, of the final product.

catalyst and heating the mixture to 700°C for over one hour in the presence of a slow nitrogen purge. The resulting yields of char, liquids, and gases were collected and analyzed.

Details of the experimental setup and some preliminary results have been reported elsewhere (Arzoumanidis et al. 1995).

4 Results

4.1 Products from Laboratory Tests

We have found that the products of pyrolysis are recovered in four distinct phases:

1. Liquid organic (Lo), consisting of a liquid at room temperature, which is conveniently classified into two fractions: a light liquid that boils below 190°C, having major components of benzene, toluene, styrene, benzonitrile, 2,4-dimethyl-1-heptene and other volatiles; and a heavier liquid that boils above 190°C, containing mostly branched aliphatics of 12 to 30 carbon atoms per molecule.

2. Aqueous liquid (La), consisting of approximately 67 weight percent water, with the balance being dissolved oxygenates — mostly acetic acid, benzoic acid, and various glycols.

3. Gases, consisting of about 50% olefins (mostly ethylene, propene, butene), 28% saturates (mostly methane and ethane), 13% CO_2, and 9% methyl chloride.[3]

4. Char, consisting of a high carbon solid of about a 1:1 carbon to hydrogen atomic ratio, inert materials, and small quantities of nitrogen and chlorine.

The Lo phase is believed to have the most potential value, either as a fuel or for its chemical content. The gas phase may be the next most valuable due to its olefin and CH_3Cl content. The oxygenates of the La phase have potential value, and the sale of char as a solid fuel may be possible. Our current main interest is in maximizing the yield of the Lo phase.

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[3] HCl from decomposition of PVC reacts with methoxy groups in wood to produce methyl chloride (Arzoumanidis et al. 1995). In cases of incomplete reaction, the gas may also contain HCl.

4.2 Pyrolysis Process Simulation

To aid in understanding how yield improvements can affect the economics of the process, the pyrolysis process flow diagram shown in Figure 4.1 was simulated by using Aspen Plus software. The waste feed was assumed to have the composition given in Table 3.1. The simulations assumed the same average yields of Lo, La, char, and gases that we had obtained from a large number of laboratory tests on various catalysts. These catalyst test results have been averaged and are shown in Figure 4.2; they are discussed in more detail below (see Section 4.3). The process was assumed to utilize a double rotary kiln reactor (DRK)[4] handling 200 tons per day, and the only saleable product was assumed to be Lo at 6 cents per pound (the approximate value of unrefined liquid fuel). A credit of $35 per ton was taken for waste disposal. The most significant variable was Lo yield, which ranged from about 12 to 23%.

A number of approximations were required to perform the simulation. For example, we did not optimize the fractionation for recovery of Lo and other fractions, and an average heat transfer coefficient was used to estimate reactor size. Therefore, the estimated costs are likely to fall within only ±30% of the actual costs. However, since the same methods were used throughout the study, and essentially only Lo yield was varied, these cost results, relative to each other, are considered reliable for showing the effect of Lo yield on the relative process economics. Work towards more accurate estimations incorporating detailed process designs, such as reactor sizing and optimized separations, is ongoing and will improve the absolute values of these estimates.

Figure 4.3 summarizes the economic results of the simulations, that is, the effect of Lo yield on the internal rate of return on investment and on the plant payoff time. Each point on the curve represents a different catalyst and yield distribution, as given in Figure 4.2. An improvement of yield from 12 to 23% can increase the return from 6.7 to 27.5% and reduce payoff time from 12.5 to 4.2 years. These tentative results have provided incentive to continue the laboratory catalyst testing program that we will now briefly summarize.

4.3 Effect of Catalysts on Pyrolysis Product Distribution

Many catalysts have been tested, including petroleum cracking and

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[4] Brockmeier and McIntosh (1994) discuss this reactor and its process simulation and our economic analysis in detail.

hydrogenation catalysts and oxide catalysts (such as dolomite) that are known to have beneficial effects in some cases of pyrolysis (Vassilatos et al. 1992). In general, the results from this survey indicate that inorganic oxide catalysts are the most effective in improving yield and value, relative to pyrolysis tests without catalyst.

Figure 4.2 summarizes the results relative to yield from a large number of laboratory pyrolysis tests. The objective of these tests was to discover an effective catalyst for increasing the yields of the most valuable pyrolysis products. From the figure, we see the yield of Lo is lowest for a titanium dioxide catalyst and that the yield increases progressively from 11 to 22.7 weight percent for the series of catalysts tested; this result may be of economic significance, as shown in Figure 4.3.

The following observations can be made:

1. Titanium dioxide catalyst, relative to no catalyst, produces a large yield of La at the expense of the more valuable Lo and gas phases.

2. Zinc oxide catalyst alone, relative to no catalyst, increases the yield of Lo from 14 to 19.2% at the expense of the less valuable char and gaseous products.

3. The one to one combination of titanium dioxide and zinc oxide catalyst, relative to zinc oxide alone, increases Lo from 19.2 to 20.2% and La from 15.2 to 17.3% at the expense of gases.

4. When the titanium and zinc oxide catalyst is promoted with a Cs_2CO_3 base, an improvement in Lo yield from 20.2 to 22.7%, relative to the unpromoted case, is seen at the expense of gases.

5. The calcium oxide promoted catalyst, relative to the cesium carbonate and sodium hydroxide promoted catalysts, changes La yields to gases from 16.2 (NaOH) and 15.8 ($CsCO_3$) to 13.9%.

6. Promoting zinc oxide catalyst with TiO_2 and bases has produced important Lo yield improvements, mostly at the expense of the La and gas phases, and has been ineffective in reducing the char. Additional work is needed to find a catalyst that will increase Lo yield by directing char carbon along the path to Lo formation.

4.4   Effect of Catalysts on Lo Component Distribution

Catalysts also have an effect on the distribution of compounds making up the Lo phase. Figure 4.4 shows the major products of pyrolysis. As shown, six individual compounds are produced in relatively high yields. In addition, a mixture of mostly branched aliphatic hydrocarbons of about carbon number 12 to 30 and boiling points above about 190°C are produced. These hydrocarbons we call "high boilers." The mixture of mostly aliphatics, with boiling points lower than 190°C, we call "other volatiles."

From Figure 4.4, we observe

1. The zinc oxide catalyst favors benzene and 2,4-dimethyl 1-heptene production and has only small relative effects on the production of other fractions.

2. Relative to no catalyst, the titanium dioxide catalyst strongly suppresses the formation of volatiles; from Figure 4.2, using a titanium dioxide catalyst coincides with an increase of La and a lesser decrease in char production.

3. Relative to the TiO_2, none, and ZnO cases, the mixture of zinc and titanium oxide catalysts in all four cases improves the yields of 2,4-dimethyl-1-heptene. In three cases out of four, the mixture increases the high boiler yield. In the fourth case, the high boiler yield is suppressed and the other volatiles yield is enhanced by calcium oxide promotion.

4. Promotion with cesium carbonate gives the best yield of Lo, mostly due to increasing high boiler concentration.

4.5 Potential Values of Separating Individual Chemicals

The high yields of individual chemicals observed in Figure 4.4 suggest the intriguing possibility of separating these chemicals and selling them at the current market price. Separation of the Lo type of liquid can be done by coupled distillation and extraction (Sulfane Process). Based on our Aspen Plus process studies, we conclude that these liquids can be separated by the process shown in Figure 4.5. The Figure 4.5 flowsheet incorporates the same pyrolysis process that is given in Figure 4.1 but also includes the separation equipment. This flowsheet has been simulated and the economics have been estimated using Aspen Plus for the $ZnO/TiO_2/Cs_2CO_3$ case. Table 4.2 shows the yields of benzene, toluene, benzonitrile, and styrene/ethyl

benzene[5] for this case, along with their current market values (*Chemical Marketing Reporter* 1996). Thus, if all the other chemicals of the Lo phase are considered to be worth 6¢/lb, the weighted additional value of these separated chemicals gives an overall value of 9.62¢/lb for the Lo phase.

Accurate estimates of economics will require better reactor cost estimates and optimized separations, as discussed above. However, on the basis of our current estimates, which include additional costs relative to the Figure 4.1 case because of separations, the interest rates of return for various selling prices of Lo have been estimated. These data are plotted in Figure 4.6. The return for a selling price of 9.62¢/lb is still a relatively attractive 23%, in spite of the additional costs of separation. This result provides incentive for continuing catalyst and process economic studies of waste pyrolysis.

Note that the yields of the chemicals listed in Table 4.2 for the CaO promoted case from Figure 4.4 are higher than those reported for the Cs_2CO_3 case. These yields would produce a higher return than the 23% estimated for the Cs_2CO_3 case. These results emphasize the important effect of catalysts on yields of specific products and indicate the large number of possibilities for improving economics with catalysts.

Additional work to improve the accuracy of our process economics and to study further the potential of catalytic pyrolysis on other waste plastics is under way.

5 Conclusions

1. Binary oxide catalysts, especially ZnO/TiO_2, are effective in adjusting the yields and compositions of organic pyrolysis products obtained by pyrolyzing wastes containing mixed plastics.

2. Economic estimates based on rough process designs indicate the possibility that catalytic pyrolysis has potential economic viability and provide incentive for further studies.

6 Acknowledgment

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[5] A mixture of styrene and ethyl benzene is a marketable product useful in styrene polymer production. Our estimated value is 16¢/lb. Pure styrene is worth 32¢/lb.

7 References

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Table 3.1 Composition Of Simulated Waste Stream

Wood	31.4%
Glass-reinforced polyester	18.4%
Tar	15.7%
Polyurethane foam	10.5%
PVC	7.3%
ABS	3.7%
Nylon	2.1%
Acrylic	<u>2.1%</u>
Total	100.0%

Table 4.2 Estimated Value of Separated Organic Liquid

	¢/lb	lb/100 lb feed	Fraction in Lo	Component Value
Benzene	13.7	3.64	0.160	2.19
Toluene	11.6	1.50	0.066	0.77
Styrene + ethyl benzene	16.0	2.03	0.090	1.44
Nitrobenzene	30.0	1.07	0.047	1.41
Others	6.0	14.4	0.635	3.81
Value of Lo				9.62¢/lb
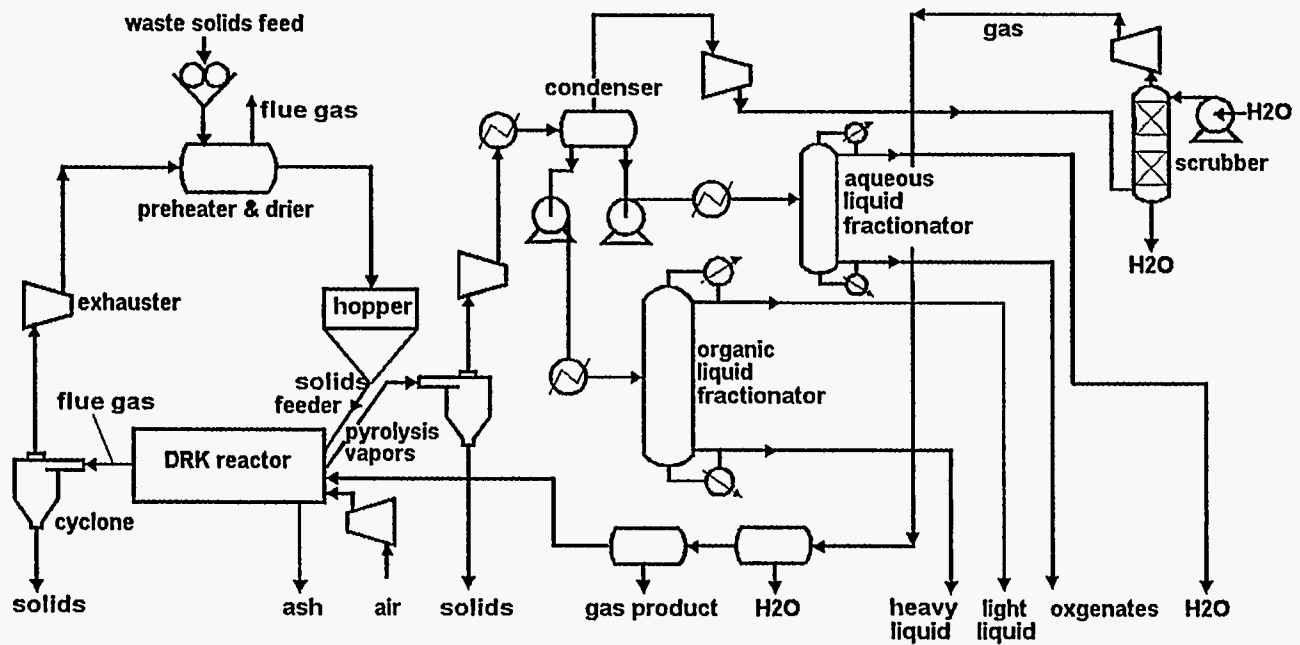
FIGURE 4.1 Pyrolysis Process Flow Diagram
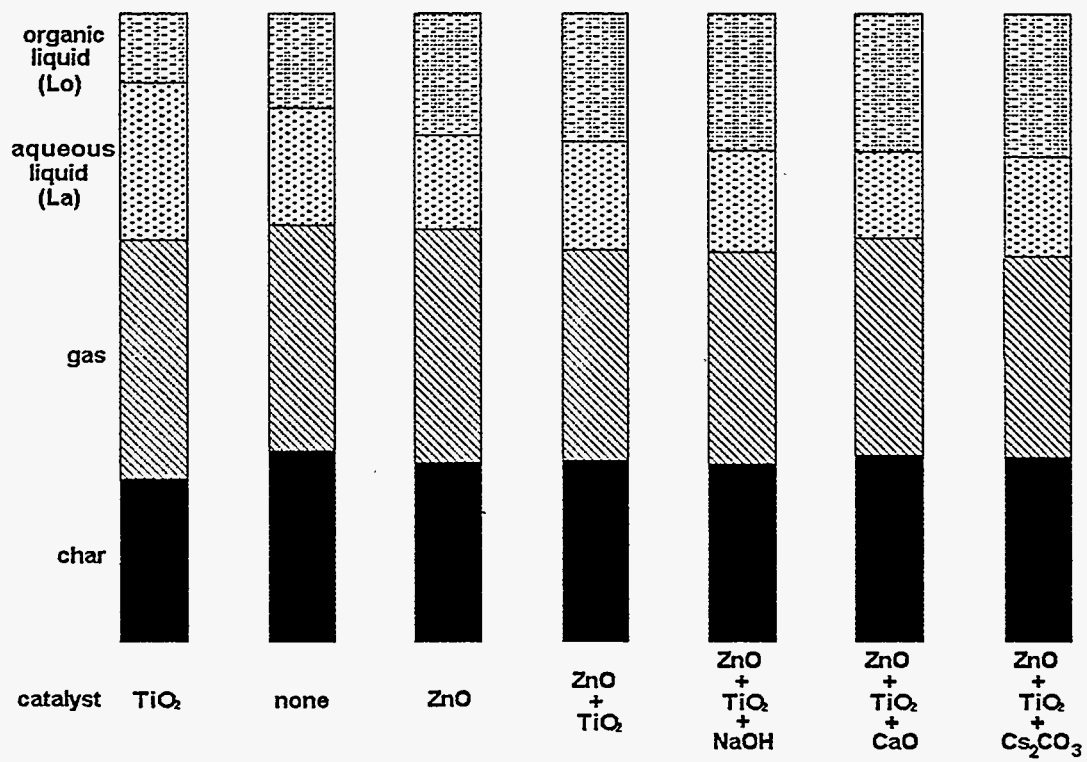
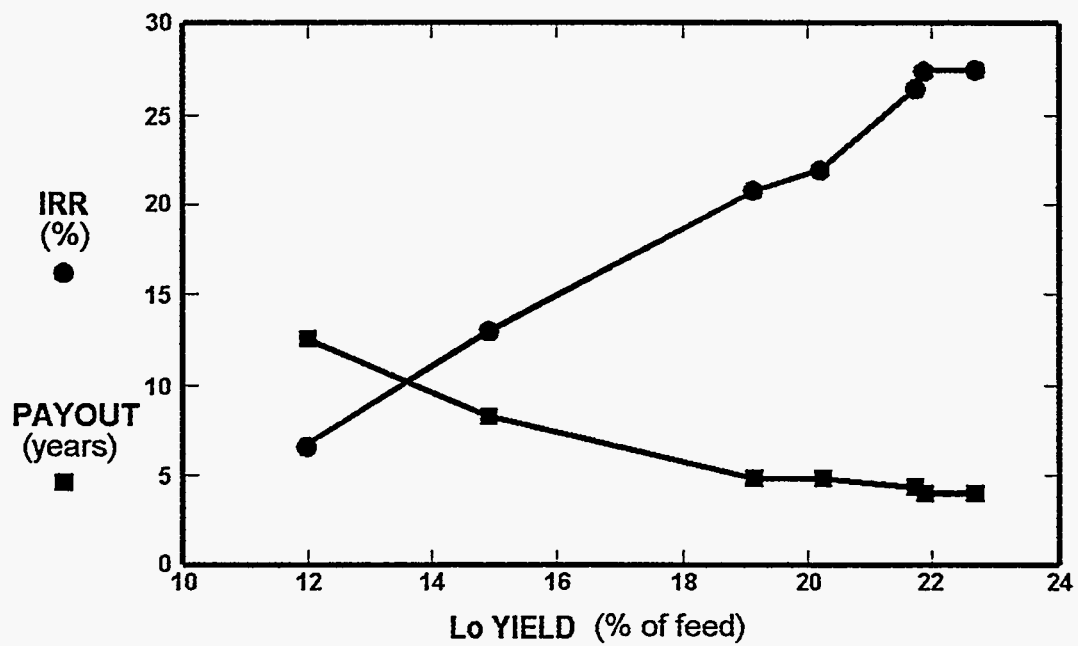FIGURE 4.2 Average Product Yields for Various Catalysts

FIGURE 4.3 Effect of Organic Liquid (Lo) Yield on the
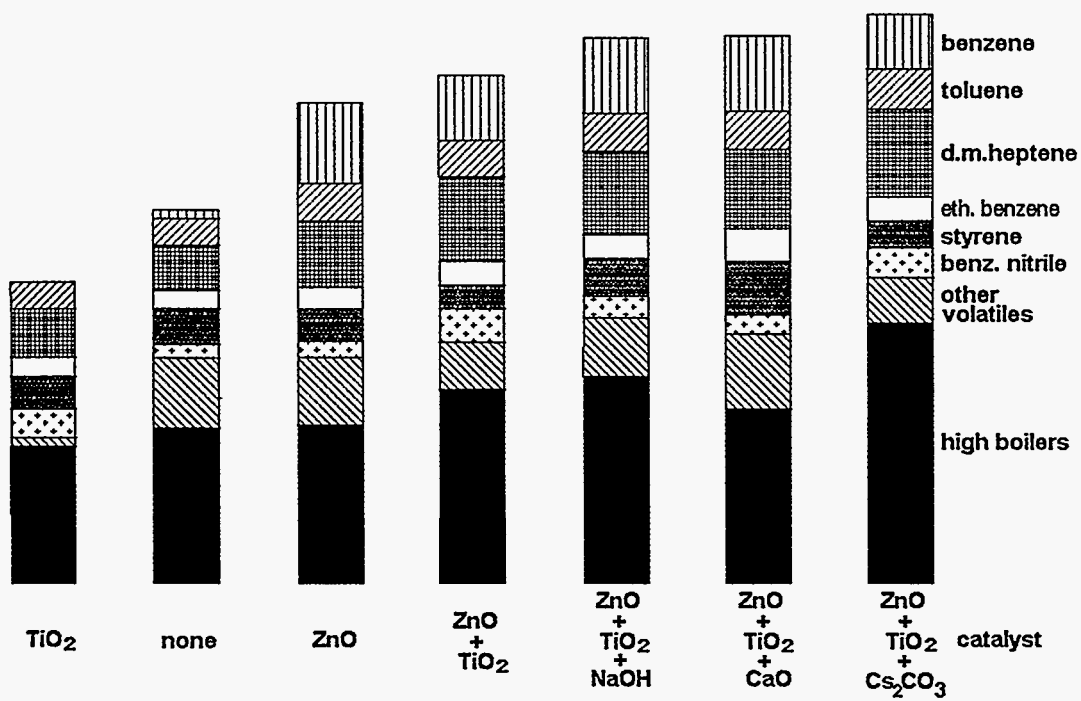Economics of a Pyrolysis Process

FIGURE 4.4 Effect of Catalysts on the Distribution of Compounds Comprising the Organic Liquid Phase (Lo)
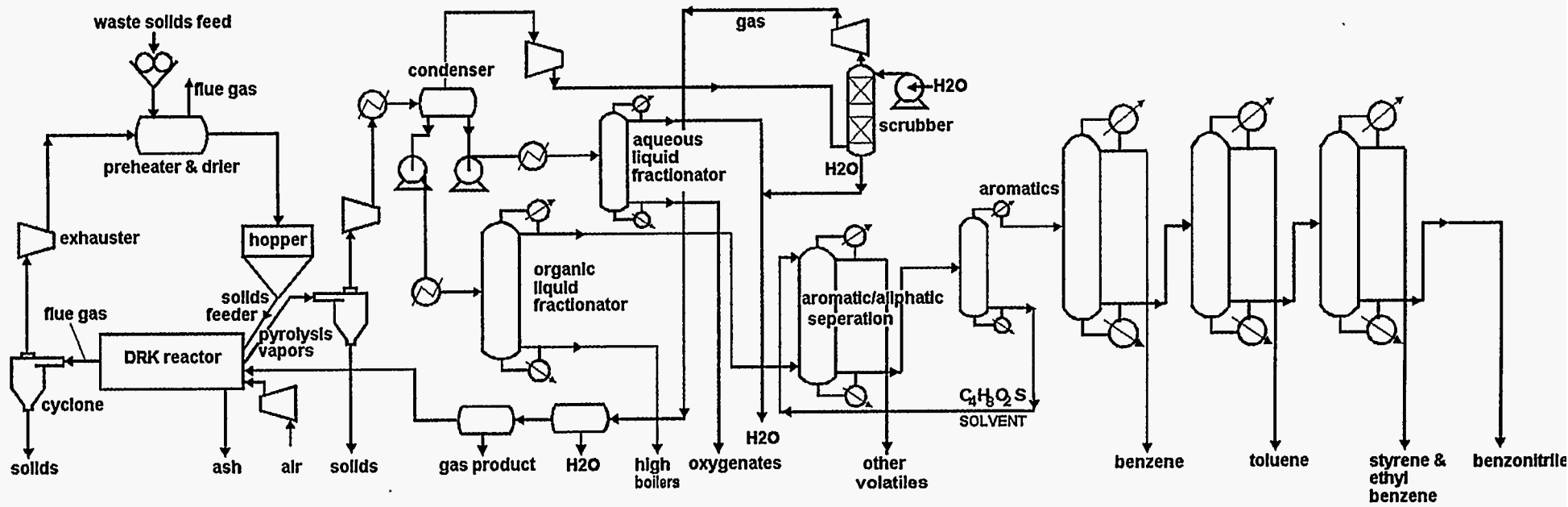
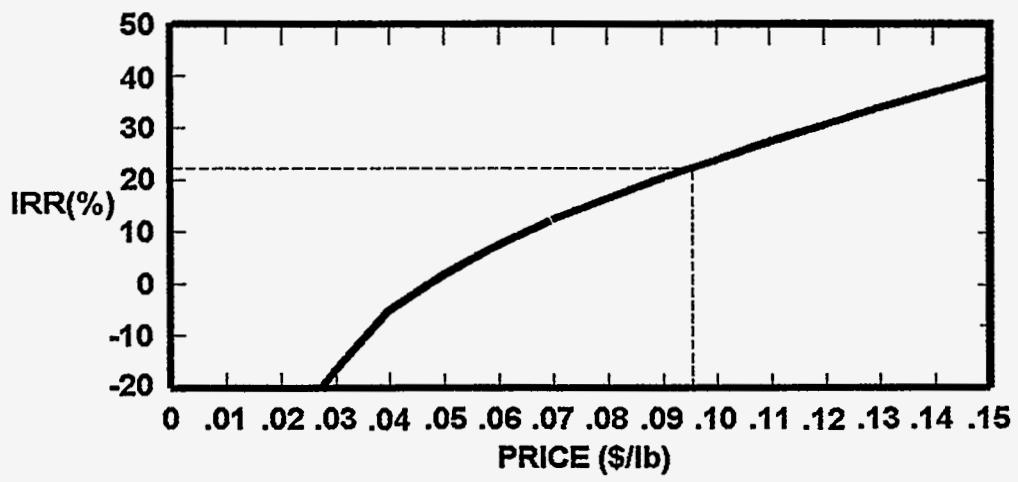**FIGURE 4.5 Pyrolysis Process with Lo Fractionation**

FIGURE 4.6 Effect of Organic Liquid Price on Pyrolysis Economics