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August 1983

The Value of Furfural/Ethanol Coproduction from Acid Hydrolysis Processes

Stephen Parker (SERI)
Mark Calnon (SERI)
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Prepared under Task No. 1372.25
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PREFACE

This report presents an evaluation of the potential of furfural, a by-product of the acid hydrolysis of cellulose, to serve as a source of revenue to offset some ethanol production costs, thus reducing the selling price of ethanol. It is one of a series of evaluations that will cover alternative acid hydrolysis processes, enzymatic hydrolysis processes, ethanol-water separation methods, and by-product production and utilization. The first report in this series is High Temperature Acid Hydrolysis of Cellulose for Alcohol Fuel Production, SERI/TR-231-1714, by John Wright, published in April 1983. All reports in this series are to be prepared for the Office of Alcohol Fuels, U.S. Department of Energy (DOE).

The approach used for this project was multidisciplinary, requiring engineering, economic, and computer modeling expertise. The resulting report format is therefore a reflection of this requirement. The process engineering analyses, performed by Lawrence Weiss of Energy Technology Associates, are reported in detail in Appendix A and summarized in Section 3.0. Computer-supported analyses were required to complete the process engineering work. The results of these analyses are reported in Section 4.0.

The authors wish to thank Bernie Neenan of the Technical Evaluation and Planning Group in the SERI Solar Fuels and Chemicals Division for his contributions and guidance during this work. Special appreciation is also expressed to Ronald Farina, the codeveloper of the PETNET model, for his many contributions to this effort.

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SUMMARY

Objective

Parametric analyses of high-temperature, dilute-acid hydrolysis of cellulose were carried out to determine the effect of hydrolysis parameters and processing schemes on the selling price of ethanol. The results of these analyses, reported in the Solar Energy Research Institute (SERI) publication High Temperature Acid Hydrolysis of Cellulose for Alcohol Fuel Production, indicate that two major process modifications could result in significant reductions in the ethanol selling price. One improvement is the development of yeasts capable of fermenting xylose (the five-carbon fraction of the cellulosic material) to ethanol. This modification would improve the process efficiency (by as much as 30%) and increase product yield. The other improvement is the recovery of process by-product furfural and the use of it as a marketable chemical product. The revenue from the sale of furfural would offset some ethanol production costs. A by-product credit for furfural could reduce the selling price of ethanol by as much as 50%, given that sufficient markets for furfural are available. This report compares the relative benefits of the two options in improving the economics of ethanol production.

Discussion

With existing acid hydrolysis process technology for converting cellulosic materials (e.g., wood, crop residues) to ethanol, production costs are too high to produce an ethanol product at a price competitive with gasoline as a neat fuel or with traditional fuel extenders and octane boosters such as methyl tertiary butyl ether (MBTE), tertiary butyl alcohol (TBA), and n-butane. Research and developmental work on this technology have focused on process improvements that could reduce the price of ethanol to competitive levels. Two potential technology modifications—xylose fermentation and the application of a furfural by-product credit—have been shown to promise the largest price reductions. Both of these proposed improvements consume the xylose fraction of the feedstock. For purposes of research and development planning, it is useful to have some idea of the relative impacts of these options in reducing ethanol production costs. Parametric analysis of these options indicates that the recovery of furfural as a by-product is more beneficial than xylose fermentation if the net profit from the sale of furfural is greater than \$0.08/lb (the 1982 chemical market value for furfural was approximately \$0.66/lb). The availability of markets for furfural, therefore, is the key factor in this comparative evaluation.

The present markets for furfural are not sufficiently large to support a large ethanol/furfural coproduction capacity. The 1982 production of furfural was approximately 140 x 10^6 lb. Considering that about 140-180 x 10^6 lb of furfural would be coproduced with 50 x 10^6 gal/yr of ethanol, the limit on "subsidized" ethanol production would be only 50 x 10^6 gal/yr.

If a furfural by-product credit is to be a viable option (i.e., subsidize a large ethanol production capacity), new chemical markets for furfural must be identified. The MITRE Corporation addressed this problem in their January 1983 report, Chemicals from Wood: The Policy Implications of Federal Subsidy. MITRE concluded that the most likely level of market penetration by furfural in 1990 would be 440 x 10^6 lb/yr coproduced with an ethanol production of 150 x 10^6 gal/yr. However, the MITRE furfural estimate was linked to, and therefore limited by, their projection of ethanol production potential. The market penetration potential of furfural in chemical markets could be much greater than 440 x 10^6 lb/yr. MITRE suggests that at furfural prices approaching \$0.30/lb, vast markets (approaching 2 x 10^9 lb/yr) could potentially open up for furfural. However, they state that to define more accurately that potential, detailed engineering, economic, and market analyses would be required. For the study described in this report, a methodology was devised that incorporates the levels of analyses necessary to make a credible estimate of the market potential of by-product furfural.

The methodology consists of the following steps:

(1) Survey of the existing literature concerning the upgrading of furfural. From this survey, furfural processes are identified that have potential to displace hydrocarbon-based chemical production processes.

(2) Selection of furfural-based processes to study. A comprehensive analysis of all furfural substitution possibilities is a formidable task and exceeds our time and resource constraints. Therefore, specified criteria are used to select the furfural processes.

(3) Technical and economic feasibility assessment. All furfural-based routes identified in this study have been investigated only on a laboratory scale. Process studies are made of competing furfural-based and conventional routes to the production of the chemicals selected for study. Comparisons of the capital and operating costs for competing process options provide a preliminary indication of the potential for furfural to displace petroleum feedstocks in petrochemical markets and to subsidize the price of ethanol for fuel markets.

(4) Petrochemical market analysis. A competitive cost advantage for a furfural-based process will not ensure that it displaces the existing, hydrocarbon-based process. There are complex factors inherent in the petrochemicals industry that can restrict the market penetration by a new source. A computer model of the petrochemical industry is used to determine if the new competitive furfural processes will actually be utilized and to determine the impact of revenues from the sale of furfural on the selling price of ethanol.

Conclusions

The process engineering studies involved the design of processes utilizing furfural as the primary input that can be compared to the conventional hydrocarbon processes for producing butanol, butadiene, adipic acid, maleic anhydride, and styrene. The designs for styrene and butadiene were found to be marginally competitive or not competitive even with furfural prices set at zero. No further analysis was done with these two processes. The designs for adipic acid, maleic anhydride, and butanol generated selling prices equal to the competitive hydrocarbon processes when furfural was priced at \$0.29/lb, \$0.10/lb, and \$0.08/lb, respectively.

The subsequent computer analysis of furfural potential, in the context of an optimally organized petrochemical industry, indicates that these three promising processes could subsidize approximately 900 x 10^6 gal of ethanol to a selling price below \$1.00/gal. If additional furfural markets of about 5 x 10^9 lb, with a value of at least \$0.08/lb, could be identified, then over 2.5 x 10^9 gal of ethanol could be marketed at about \$1.00/gal. The phenolic resin market is another possible outlet for large quantities of furfural. Current domestic volume is 1.2-1.5 x 10^9 lb/yr with prices in the \$2.00-\$2.50/lb range. The market has been dominated since its beginning by phenol-formaldehyde formulations and has become firmly established on this foundation. Furfural (an aldehyde) can be substituted for formaldehyde to yield a different group of thermo-setting phenolic resins. A related potential new product group could be furan resins, based on substitution of furfuryl alcohol (from furfural) for phenol. A large number of formulations were invented many years ago, but they remain undeveloped. It is possible that, given very low cost furfural, a new competitive link of phenolic resins would find a place in the market. However, estimates of such penetration are difficult to estimate because of the complex interactions of formulations, performance properties and prices, and the traditional and strong resistance of the resin business to changes. Investigation of the place of furfural in the thermo-setting resin business was beyond the scope of this study, but could be done as a separate future project. Process technology and marketing studies would necessarily be considerably more extensive than in the relatively straightforward appraisals of commodity chemicals in this study.

Converting the xylose stream to ethanol decreases the cost of production by about $0.30/gal, resulting in up to 3×10^9 gal of ethanol subsidized to about $1.00/gal. Thus, the greatest ethanol production will result from xylose fermentation, while the furfural credit offers large near-term profits as an incentive to investors and has a more diversified impact on reducing petroleum product demand.

Lignin is another potentially high-value by-product of cellulose hydrolysis. The potentially most important lignin derivatives are phenol and benzene. Future ethanol process studies of technology economics and market potentials and work on furfural development should include consideration of the contribution of lignin and its derivatives.

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SECTION 1.0

INTRODUCTION

The conversion of cellulosic materials to ethanol by means of acid hydrolysis is currently the subject of intensive research and development. The focus of this effort is on lowering production costs in order to reduce the selling price of ethanol to a level competitive with gasoline as a neat fuel or with more traditional fuel extenders and octane boosters such as methyl tertiary butyl ether (MTBE), tertiary butyl alcohol (TBA), and n-butane. Parametric analyses performed using an acid hydrolysis simulation model indicate the potential for ethanol price reductions that would achieve cost-competitiveness (Wright 1983). Two modifications in the technology, shown to result in the largest price reductions, are the focus of this report.*

The first major improvement identified is the development of yeasts or bacteria capable of fermenting five-carbon sugars to ethanol. Xylose (the source of the five-carbon sugars) may account for up to 30% of the sugar content in the lignocellulosic feedstock and 50% of the recoverable sugar. Xylose cannot be fermented to ethanol with the yeasts currently used in industry. As a result, ethanol yields are relatively low and conversion costs are too high to produce ethanol at a price competitive with conventional fuels. The development of xylose fermentation technology could reduce the cost of ethanol 30% to approximately $1.00-$1.10/gal; this price greatly enhances the potential use of ethanol as a transportation fuel.

The second approach involves the use of furfural as a source of revenue to offset some ethanol production costs (i.e., to provide a by-product credit). If a prehydrolysis step is not incorporated into the acid hydrolysis process, the five-carbon sugars are degraded into other products, primarily furfural. In initial process development work, furfural has been considered a waste product. However, it has the potential to be a valuable by-product. A furfural by-product credit could substantially reduce (subsidize) the selling price of ethanol. For example, a net credit** of $0.15/lb of furfural would reduce the selling price of ethanol from $1.60/gal to approximately $0.80/gal, a 50% decrease (Wright 1983).

While either option has potential for reducing ethanol costs, both of these proposed improvements consume the xylose fraction of the feedstock: the options compete for the same substrate. Determining which option has the greatest potential impact on the economics of ethanol production is important in establishing research priorities. If one option is more economically viable than the other, that option is a preferred R&D strategy. Parametric analysis of these options (Wright 1983) indicates that the recovery of furfural as a by-product from a system with no prehydrolysis step is more beneficial than xylose fermentation if the net profit (i.e., net credit) is greater than $0.08/lb of

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*Increasing the solids concentration in the reactor feed is a third source of potentially large selling price reductions.

**A net credit, in this case, is the difference between the cost of producing the furfural and its selling price. The credit to the ethanol selling price is related to the particular plant design and size and to feedstock costs. Thus, while approximately 3.5 lb of furfural are produced per gallon of ethanol, the credit or subsidy relationship is not linear except with a specific plant design and for given prices of all other inputs.

furfural. The key factor in this comparative evaluation is, therefore, the availability of markets for the furfural by-product. If markets for quantities of furfural sufficient to provide a credit that can be sustained for a substantial ethanol production capacity are not available, or cannot be easily penetrated, the future research focus should be on improving xylose fermentation to provide long-run supplies of ethanol competitive with hydrocarbon-based transportation fuels.

An initial examination of the current furfural market does not reveal a very promising situation. The present domestic consumption of furfural is about 100 x 10^6 lb/yr, and the demand is increasing very slowly (Johnson 1983). Quaker Oats is the exclusive producer of the domestic furfural supply and is responsible for nearly half of the annual world production. Despite their current dominance of this market, Quaker Oats may not remain in a competitive position if a source of low-priced furfural is developed. The current value of furfural in the chemicals market is $0.66/lb (Chemical Marketing Reporter 1983, p. 42). Furfural can provide a valuable by-product credit for ethanol production at a price well below the current market price of furfural. As promising as this competitive situation might seem to prospective ethanol producers, investment opportunity would be limited by the size of the market. Considering that approximately 145 x 10^6 lb of furfural would be coproduced in a 50 x 10^6 gal/yr ethanol plant, the limit on "subsidized" ethanol/furfural coproduction would be reached upon construction of the first large-scale plant (i.e., only production of 50 x 10^6 gal/yr of ethanol would be subsidized by a furfural credit).

With such limitations associated with the current market, subsidizing a large ethanol production capacity involves identifying other chemical markets that furfural might penetrate and evaluating the market potential. The most comprehensive study of this problem to date was performed by the MITRE Corporation and presented as a section of their January 1983 report, Chemicals from Wood: The Policy Implications of Federal Subsidy (Johnson 1983). As a prerequisite for their policy analysis work in this study, MITRE performed market penetration studies for five large-volume industrial chemicals derived from wood: ethanol, furfural, phenol, methanol, and acetic acid. The total market for each chemical was estimated for the year 1990, and these projections were the basis for examining the existing and potential markets for furfural. MITRE concluded that the most likely level of market penetration would be 440 x 10^6 lb at prices between $0.30-$0.35/lb. This volume of furfural, coproduced with, and constrained by, MITRE's estimated wood-derived ethanol production of 150 x 10^6 gal, results in a projected four-fold increase over the current market, a seemingly promising projection. However, the implied ethanol production suggests a limited growth potential for cellulose-to-ethanol production without extensive cost reductions in other areas (e.g., C_5 sugar fermentation). In terms of the question of "subsidization" of ethanol production, MITRE's projections indicate a market situation in which a furfural subsidy will be available for the production of 150 x 10^6 gal of ethanol per year, the output of only three large-scale plants.

Although the MITRE estimates lend valuable perspective to the question of "downstream" research priority, there is not sufficient information for a research decision. The MITRE furfural estimate was necessarily linked to, and therefore limited by, the projection of ethanol production potential. Indeed, MITRE does suggest, in reference to their Exhibit 4.6, that in a range of prices, somewhere between the current price of $0.66/lb and about $0.30/lb, vast markets (perhaps approaching 2 x 10^9 lb/yr) could potentially open up for furfural (Johnson 1983). They state, however, that detailed engineering, economic, and market analyses would be required to accurately define that potential. In light of the importance of a sustained furfural by-product credit to the economic viability of cellulose-to-ethanol production technology, it appears worthwhile to carry out the analyses required to arrive at a more definitive answer.

An assessment of the technical structure of the U.S. petrochemical industry by Rudd et al. (1981) offers insight into additional complexities that arise in evaluating the industry's potential for changing production practices. The study did not address furfural potential directly, but the results of an analysis of the impacts of large supplies of fermentation ethanol demonstrate the need for evaluating the entire industry structure, even when only a single process substitution is of immediate concern.

Rudd et al. constructed an economic model of the petrochemical industry that included 182 processes for transforming 131 feedstocks and intermediates to chemicals (Rudd et al. 1981, p. 36). As modeled, the industry seeks to utilize available processes and feedstocks to meet demands at a minimal cost. Included among the alternative processes were several that could use fermentation alcohol as an intermediate to displace ethanol derived from ethylene. To examine the potential role of alternative alcohol technologies, the model was examined for the impacts of an unlimited supply of alcohol at various prices; these prices were defined as percentages of the projected 1985 price of ethanol for industrial uses.*

The results of this parametric analysis in which a single chemical price—that of ethanol—was varied demonstrate how multilevel adjustments result from one stimulus. At the full projected 1985 ethanol price, both the feedstocks and the products of ethanol production are affected. Ethylene consumption falls by 3% as a result of more favorable economics for fermentation-based ethanol over the conventional ethylene-to-ethanol route. In addition, gas oil becomes a more attractive feedstock for ethylene production and the 8% increase in its consumption causes a 5% drop in propane consumption (for ethylene production). The change in feedstock usage, triggered by the change in the relative fermentation alcohol price, is the first of several secondary impacts reported by Rudd et al.

If the price of ethanol is 40% of the projected price, a process using alcohol to produce acetaldehyde replaces ethylene oxidation. At the 35% price level, lower-cost acetaldehyde (from alcohol) becomes an attractive feedstock for teraphthalic acid (TPA), which in turn displaces production of acetic acid from methanol because acetic acid is a by-product of TPA production. Even more substitutions can result from the joint-product nature of TPA production. The old TPA route, which utilizes methyl ethyl ketone (MEK), is no longer economically attractive, freeing n-butenes for use elsewhere, including displacement of n-butanes in butadiene production. The outcome of the initial change in the production of TPA, triggered by a change in ethanol price only, is finally felt in butadiene production.

The multiple-level adjustments resulting from changes in the ethanol price are indicative of the complex, integrated structure of chemical production. The by-product relationships are extensive, and the interdependencies among processes are complex. Only by modeling the complex technical and price interrelationships is it possible to anticipate the full impact of changing technology and price relationships on the petrochemical industry.

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*Rudd et al. report the model results for parametric analysis of ethanol prices over the range of 0% to 100% of the projected 1985 price but do not indicate what that price is.

Recent studies highlight the important factors to be considered in evaluating acid hydrolysis technology. Wright's (1983) analysis points out the need to assess alternative, competing uses of the xylose portion of cellulosic feedstocks. The MITRE (1983) report demonstrates the limited potential for furfural subsidies in the existing industrial structure, but it mentions only briefly alternative technologies and possible extensions of the credit, albeit at lower levels, to a greater volume of ethanol. Finally, the analysis of Rudd et al. (1981) shows the complicated actions and reactions that can arise from changing the economic and technical environment within which the petrochemical industry operates.

This report establishes the basis, through the development of the necessary analytical tools and procedures, for a more thorough examination of the market capture potential of furfural. The full range of market possibilities is too extensive to examine credibly in a limited time-frame. Therefore, for a detailed study the SERI research team has chosen five, large-volume commodity chemicals that can be produced from furfural instead of hydrocarbon-based resources. We propose that the analytical methods developed and used in this study be applied to an exhaustive examination of the full spectrum of potential furfural derivatives.

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SECTION 2.0

APPROACH

This study is an extension of earlier MITRE Corporation work (Johnson et al. 1983) that presented pro forma economics and market penetration estimates for 1990 of five chemicals potentially produced from wood but now made by established hydrocarbon-precursor processes: ethanol, furfural, phenol, methanol, and acetic acid. The MITRE results indicated, subject to a number of complex qualifications, that wood does show long-term promise as a chemical feedstock. The broad scope of the MITRE investigation has, for this study, been focused on furfural and the economic potential of five selected derivatives that would displace, over a somewhat longer term, hydrocarbon-based chemicals. The relatively limited objective is to determine the value of by-product furfural to the cellulose hydrolysis process of ethanol production. This is determined by estimating equivalent furfural prices that would allow furfural-process operations to be as profitable as conventional hydrocarbon-process routes, in 1995, in the large-scale manufacture of butanol, butadiene, styrene, adipic acid, and maleic anhydride. The year 1995 represents the earliest date that the furfural derivatives studied could come on stream as commercial operations. The year in which all of the differential economics calculations for hydrocarbon versus furfural processes are based is 1995. The focus is on differentials in a realistic time frame, not on absolute values. To reduce a 1995 dollar value to a 1982 value, divide by 2.225. See Table A-7 in Appendix A for a tabulation of 1982 and 1995 raw materials prices. The study is conservative because the potential added by-product values of chemicals from lignin, such as phenol and benzene, and resin formulations containing furfural and lignin, were not considered. Additional work would be required to appraise the full economic potential of all by-products in the cellulose hydrolysis ethanol process; this study looks only at furfural.

As stated in Section 1.0, research has identified two major routes to market penetration by furfural derived from acid hydrolysis in chemicals markets. The first route is through cost competition for the existing final demand for furfural. That demand is being met exclusively by furfural produced by the Quaker Oats Company. With the introduction of furfural coproduced from the acid hydrolysis of cellulose, there will be competition for that furfural market. The key factor in determining the conditions for and rate of production will be the production cost differential between the competitive sources. If furfural derived from acid hydrolysis can be produced at a lower unit cost and in sufficient quantity to meet demand, it will likely displace current production. However, the existing furfural market is mature, relatively small, and growing slowly, limiting the subsidy potential of a furfural by-product credit for ethanol production (Johnson 1983).

The second route to furfural market penetration, and the one on which we concentrate in this study, involves upgrading furfural to derivatives that can substitute for current petrochemical feedstocks or intermediates in the production of existing commodity chemicals. The assessment of furfural market penetration potential by this route is more difficult than assessment of the existing furfural market. One reason is that the technical and economic feasibility of production routes to furfural derivatives has not been established. The other, more significant reason is that the complex, product-interrelated structure of the petrochemical industry can impose constraints on the introduction of new feedstocks or modes of production. For this study, therefore, we have selected distinct yet complementary analytical methods that take into account the engineering, economic, and market factors required to arrive at an informative assessment of market potential.

The analytical foundation of this report is the process engineering analyses of the hydrocarbon- and furfural-based routes to the production of the five large-volume commodity chemicals studied in this report: butanol, butadiene, styrene, adipic acid, and maleic anhydride. Other selection criteria were (1) availability of well-defined process technology and capital-operating cost data for large-scale hydrocarbon-route plants, (2) availability of patent and laboratory experimental data on furfural-route processes, (3) high probability of ultimate successful commercial-scale development of furfural-based processes, and (4) a history of a least ground-breaking research work on the selected furfural processes in Germany and England in the 1930s. As described in Section 3.0, comparisons of the capital and operating costs for competing process options provide a preliminary indication of the potential for furfural to displace petroleum feedstocks in these markets and to subsidize the price of ethanol for fuel markets.

The cost comparisons were derived by first calculating the sales price for 15% discounted cash flow (DCF) return for the hydrocarbon-based routes. Then, for the furfural routes the raw materials costs were calculated to yield the same DCF returns as the hydrocarbon routes. Finally, the equivalent furan/tetrahydrofuran and furfural costs were calculated. These furfural costs, less estimated recovery costs of about $0.03/lb,* are approximate measures of the respective by-product values that could be credited to the cellulose hydrolysis ethanol process. The results constitute a conservative base case and may be modified, if desired, for various inflation rates and future crude oil market values. The 1995 OPEC market crude FOB price used in this study is $67.00 per barrel.

The results of this first level of evaluation, which analyzes the cost differential between the established production processes and the proposed furfural-based processes, provides an initial characterization of the competitive economics and technical feasibility. However, a competitive cost advantage for a furfural-based process will not ensure that it displaces the existing process. There are complex factors inherent in the petrochemicals industry, particularly the high degree of product integration and the internal (captive) use of chemical products by manufacturers, that can restrict the market penetration by a new source. Section 4.0 discusses how the integrated structure of the petrochemical industry can be expected to affect the cost required to trigger penetration of new technologies. Then, using a model of the U.S. fuels and petrochemical industry, the potential for subsidizing ethanol production with furfural by-product credits is examined. In addition, the relative benefits of alternative R&D efforts, including expanding furfural markets and converting the xylose stream to ethanol, are evaluated.

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*Furfural recovery costs are site-sensitive because the dominant cost factor, both capital and operating, is low-pressure steam. A plant steam balance with a significant surplus of low-pressure steam is a common condition and could lead to recovery costs less than $0.03/lb.

SECTION 3.0

PROCESS TECHNOLOGY

3.1 INTRODUCTION

The upgrading of furfural to produce commodity chemicals is not a subject of exclusively recent interest. Furfural was investigated in the laboratory many years ago, especially in wartime Germany in the 1930s, as an alternative feedstock for hydrocarbon-based commodity chemicals such as butadiene, styrene, maleic anhydride, adipic acid, adiponitrile, hexamethylenediamine, butanol, synthetic lubricant polymers, and many others. Walter Reppe and coworkers appear to have been leaders in this work, and descriptions of most of their experimental work can be found in German literature and British and American technical intelligence reports. Furfural was recognized long ago as a potentially useful and versatile chemical building block, but wartime urgency and the attendant disregard for cost were needed to keep interest alive and research active. Today, we have reason to revive this work because of the potential for furfural to be a large-volume, low-cost coproduct in the production of fuel-grade ethanol from the acid hydrolysis of cellulose.

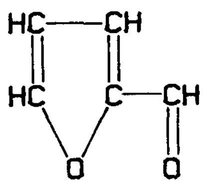
The entire spectrum of potential furfural derivatives could earn significant market shares if production costs were low enough to induce manufacturers to either add new capacity using the furfural process or replace existing hydrocarbon-based facilities. However, a comprehensive analysis of all furfural substitution possibilities in the petrochemicals industry is a formidable task and exceeds our time and resource constraints. Therefore, five derivatives were selected for study of differential costs and profitabilities. The five existing commodity chemicals, each with a production volume of at least 100×10^6 lb/yr, include adipic acid, butadiene, styrene, butanol, and maleic anhydride. In each case, an alternative, embryonic furfural process exists, as described either in old patents (mostly German) or in the literature. In all cases, considerable additional research and development work will be needed to define adequate commercial plant projects.

This section presents a first level of analysis of the market feasibility of these furfural derivatives. Background information relevant to the analysis is provided in Sections 3.2 and 3.3. Section 3.2 introduces furfural as a biomass-derived chemical and summarizes its present markets and uses. Current market information and production data for the five commodity chemicals selected for study are presented in Section 3.3. Section 3.4 provides an overview of the assumptions used in the engineering studies performed by Energy Technology Associates. These detailed analyses of the hydrocarbon and furfural-based production routes to each chemical are summarized in Section 3.5. A full text of the analysis is available as Appendix A. Comparisons of the capital and operating costs and resulting sales prices for each competing route provide a preliminary indication of the feasibility of capture by the furfural derivatives of the five markets currently held by petrochemicals.

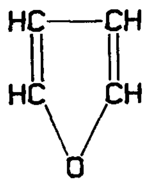
3.2 FURFURAL: CURRENT STATUS

Furfural is the common name for 2-furaldehyde, a derivative of furan. Furfural is a widely used chemical intermediate, but unlike many chemical intermediates a competitive hydrocarbon-based process for its production has never been found (McKillip and

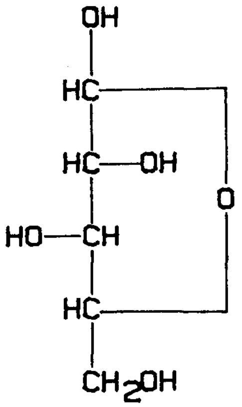
Sherman 1978). Instead, it is produced from the five-carbon sugars, especially xylose, which make up 25% or more of the composition of various woods and crop residues. The



FURFURAL



FURAN



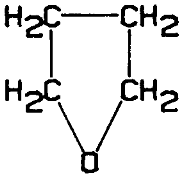
XYLOSE

Quaker Oats Company produces essentially the entire U.S. output, using oat hulls as the primary raw material (Brownlee and Miner 1948). Estimates of 1980 furfural production range from 125 x 10^6 lb (Johnson 1983). Furfural production in recent years has been only marginally profitable for Quaker Oats. The company has publicly expressed doubts about whether it will continue to produce furfural (*Chemical Marketing Reporter* 1982). The current list price of furfural is $0.66/lb (*Chemical Marketing Reporter* 1983, p. 42).

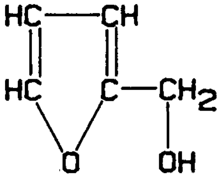
In the acid hydrolysis of a cellulosic feedstock (wood, wood wastes, or crop residue) for production of ethanol, furfural can be coproduced in yields up to 60% of the hemicellulose, or about 3.65 lb for each gallon of ethanol. A yield of 60% was used as the basis of this study. (Hydroxymethyl furfural [HMF], another by-product of less importance, was not considered in this study.) The hydrolysis reaction conditions are similar to those under which furfural is commercially prepared. Temperatures are 250°-350°C, pressures are above 100 lb/in^2, and dilute mineral acid (usually sulfuric but sometimes hydrochloric) is present (Brownlee and Miner 1948). This means that furfural is produced for only the cost of recovering and purifying it. Each plant producing 50 x 10^6 gal/yr of ethanol would also produce an amount of by-product furfural equal to the total current domestic production. Thus, the need arises for investigation into potentially suitable processes for deriving profitable end products from furfural.

At its current price, furfural has been confined to a few specialty solvent, resin, and chemical intermediate markets, most of which are expected to grow very slowly, if at all (e.g., steel) (Johnson 1983, pp. 4-26). Slight decreases in the price of furfural would directly affect its two most common derivatives, tetrahydrofuran and furfuryl alcohol. The former is an important solvent for which there is a competitive petroleum-based synthesis; furfuryl alcohol is used in the manufacture of resins and binders.

However, cheap furfural offers the most promise as a chemical intermediate. It can be and has been converted to a great variety of chemicals, some commercially and others in the laboratory only. Some of these derivatives have current markets many times that of furfural, and these markets will grow at least at the same rate as the economy. The five commodity chemicals selected for this study represent a good cross section of the



TETRAHYDROFURAN



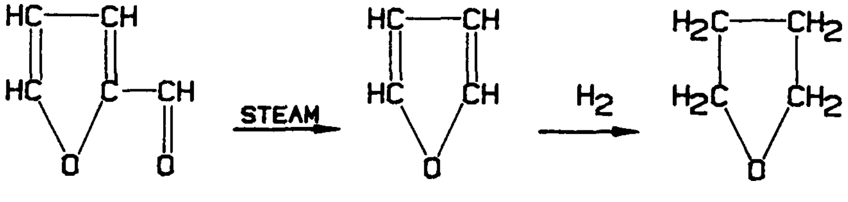
FURFURYL ALCOHOL

petrochemical industry. Each is a moderately to extremely large volume commodity chemical that is currently produced from petroleum-based feedstocks but can also be made from furfural. Each of the furfural conversion processes has been demonstrated in a laboratory.

3.3 CHEMICALS SELECTED FOR STUDY

A brief introduction to each of the five chemicals selected for study is presented in this section. The major intermediate or end uses of each chemical are highlighted and the current methods of production (and past methods where relevant) are discussed. Production data for the five chemicals are reported as a range of values, with the highest value most frequently reported from 1979 and the lowest values from 1981 or 1982, reflecting the market downturns that have affected the chemical industry. In addition, the alternative, furfural-based route to each chemical is summarized to provide necessary background for the process study summaries that follow in Section 3.5.

In each case there is a transition precursor, either furan or tetrahydrofuran (THF), derived from furfural in the following sequence:

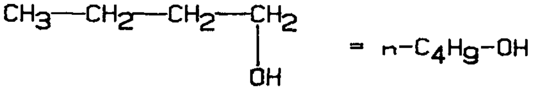


FURFURAL FURAN TETRAHYDROFURAN

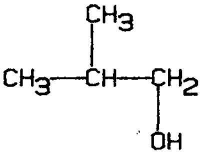
The processes are commercial, well developed, almost quantitative in conversions, and the value equivalence among the three materials is known with good accuracy. The raw materials cost estimates are expressed in terms of both the applicable intermediate (furan or tetrahydrofuran) and furfural. Note that weight losses are involved in these conversions. For example, 1 lb of furan is theoretically equivalent to 1.41 lb of furfural; the furfural-to-THF ratio is 1.33.

3.3.1 Butanol

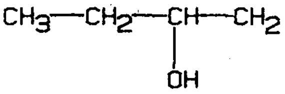
Of the four butyl alcohols, or butanols, normal butanol (n-butanol) has the longest history of commercial production and use. It was initially a product of fermentation, but for many years it has been made from hydrocarbon feedstock (Sherman 1978). Isobutyl alcohol, sec-butyl alcohol, and tert-butyl alcohol are the other, less important isomers. Tert-butanol is a legal ethanol denaturant and a patented antiknock additive for gasoline. In the absence of other specifics, "butanol" or "butyl alcohol" refers to n-butanol. Butanol has a long history of solvent use; it is also converted to lacquer solvents—butyl acetate, butyl acrylate, and butyl methacrylate. Butanol currently sells for \$0.33/lb (Chemical Marketing Reporter 1983, p. 39). Annual production is 820 x 10^6 lb (Chemical and Engineering News 1982). Tetrahydrofuran has been directly converted to butanol in the laboratory (Smith and Fuzek 1949). An important feature of this conversion is the selectivity of the reaction. Because only n-butanol is produced, purification is much simpler and less expensive. The current primary commercial route is the oxo process, using propylene derived from natural gas or petroleum.



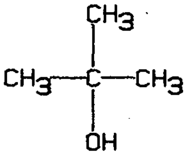
n-BUTANOL (n-BUTYL ALCOHOL)



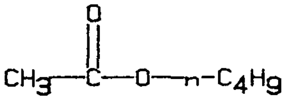
ISOBUTYL ALCOHOL



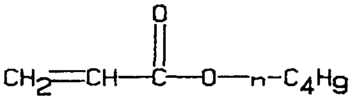
sec-BUTYL ALCOHOL



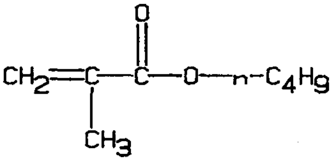
tert-BUTYL ALCOHOL



BUTYL ACETATE



BUTYL ACRYLATE



BUTYL METHACRYLATE

3.3.2 Butadiene

Butadiene is the primary component of many forms of synthetic rubber. Its peak domestic production, in 1978 and 1979, was over 3.5×10^9 lb; production was below 2×10^9 lb in 1982 (Chemical and Engineering News 1982, 1983). Over half of this butadiene is combined with styrene (see Section 3.3.3) to form styrene-butadiene rubber (SBR) and acrylonitrile-butadiene-styrene (ABS) resins. Butadiene is also converted into other synthetic rubbers, both by itself and by reaction with other chemicals, and is an important precursor for other chemicals. Butadiene has been produced by several methods. Currently it is produced primarily as a coproduct in naphtha-cracking ethylene plants. The primary feedstocks in current use are butane or butenes available from petroleum refinery light-end fractions. Interestingly, butadiene was first produced commercially from ethanol (Gilliland and Lavender 1944). Synthesis from furfural involves decarboxylation to furan, then hydrogenation to tetrahydrofuran, and finally dehydration-dehydrogenation to butadiene (Hasche 1945). At least 1.78 lb furfural are required to produce 1 lb of butadiene, which currently sells for \$0.31-\$0.34/lb (Chemical Marketing Reporter 1983, p. 39).

$CH_2{=}CH{-}CH{=}CH_2$

1,3-BUTADIENE

$CH_3{-}CH_2{-}CH_2{-}CH_3$

BUTANE

$CH_2{=}CH{-}CH_2{-}CH_3$

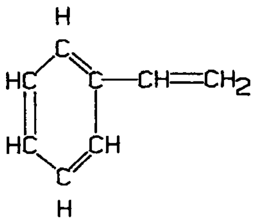
1-BUTENE

$CH_3{-}CH{=}CH{-}CH_3$

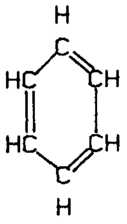
2-BUTENE

3.3.3 Styrene

Styrene, or vinylbenzene, is structurally a derivative of benzene. The primary route to styrene is a two-step process starting with benzene, a coproduct in a number of refinery processes. Ethylbenzene is produced by alkylation with ethylene, followed by dehydrogenation to styrene. Recent domestic production of styrene has ranged between 6 and 7.5×10^9 lb/yr (Chemical and Engineering News 1982, 1983). Over half is used in the

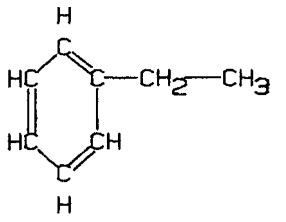


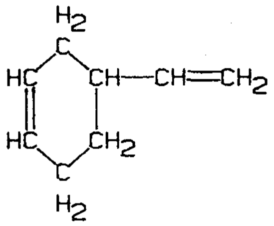
STYRENE



BENZENE

manufacture of polystyrene plastics. Another third is used in synthetic rubber and ABS resins. Ethylbenzene, and thus styrene, can be made from 4-vinylcyclohexene, which has

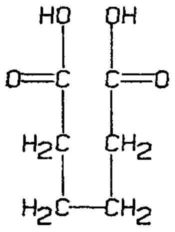

ETHYLBENZENE

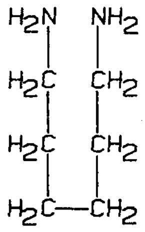

4-VINYLCYCLOHEXENE

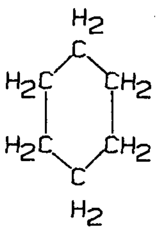
been produced in the laboratory from butadiene by the Diels-Alder reaction (Kirshenbaum 1978). With two molecules of butadiene combining to make one molecule of styrene, a minimum of 1.85 lb of furfural is required to produce 1 lb of styrene, which currently sells for $0.30-$0.35/lb (Chemical Marketing Reporter 1983, p. 46).

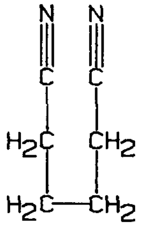
3.3.4 Adipic Acid

Adipic acid comprises half of the important copolymer synthetic fiber nylon-6,6. The other half is hexamethylene diamine. Nylon was developed in the late 1930s by DuPont as a substitute for natural fibers, marking the beginning of the synthetic fiber industry. Essentially all of the 1.2 to 1.8 x 10^9 lb of adipic acid produced each year is used for nylon production (Chemical and Engineering News 1982, 1983); very little is produced for the merchant market. This fact might hinder commercialization of new routes. The primary feedstock is cyclohexane, made by the hydrogenation of benzene. Tetrahydrofuran has been converted to adiponitrile, an adipic acid precursor, in a two-step process through dichlorobutane (Cass 1947). DuPont operated this now obsolete process for a brief period in the early 1950s. The process involved handling hydrogen chloride and hydrogen cyanide, which have undesirable hazard and high-cost features. A laboratory-demonstrated process that could be of greater interest is the one-step nickel carbonyl-catalyzed hydrocarbonylation of tetrahydrofuran, which produces high yields of adipic

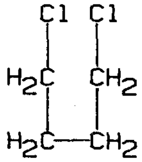

ADIPIC ACID


HEXAMETHYLENE DIAMINE


CYCLOHEXANE



ADIPONITRILE

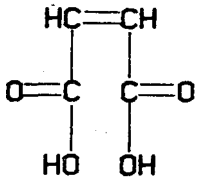


1, 4-DICHLOROBUTANE

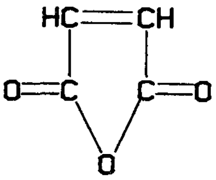
acid. (The original work was done in Germany by Reppe and coworkers British Intelligence Objectives Subcommittee [1948]). Adipic acid currently lists at \$0.57-\$0.59/lb (Chemical Marketing Reporter 1983, p. 38).

3.3.5 Maleic Anhydride

Maleic acid decomposes at about 130°-140°F to form its anhydride (to become an anhydride, a compound loses one or more molecules of water) (Milas and Walsh 1935). In an acid solution, the anhydride absorbs water to reform the acid. Maleic anhydride, with



MALEIC ACID



MALEIC ANHYDRIDE

current production between 300 and 340 x 10^6 lb/yr, is used in various unsaturated polyester resins for boat construction as well as fiberglass-reinforced plastic (FRP) tanks, piping, and electrical insulation (Chemical and Engineering News 1982). Minor uses are as a lubrication additive, food acidulant (added to increase tartness or acidity), and an agricultural chemical. The primary commercial route is based on benzene, but butane and the butenes are beginning to displace benzene. Both furfural and furan have been converted into maleic anhydride, with the latter producing better yields and fewer undesirable by-products (Milas and Walsh 1935). A minimum of 0.98 lb of furfural is required to produce 1 lb of the anhydride, which currently lists for \$0.47-\$0.56/lb (Chemical Marketing Reporter 1983, p. 43).

3.4 BASES FOR PROCESS STUDIES

A required first step in determining the market feasibility of furfural derivatives is establishing a standardized means of comparing the furfural-based routes with the hydrocarbon-based routes producing the five chemicals selected for study.

Process and economic studies performed by Energy Technology Associates (ETA) provide a comparison of capital and operating costs for the alternative processes associated with large-scale manufacture of the five chemicals under consideration. These studies allow appraisal of the economics with the best process information available. The plant capacities selected are so-called "world-class" size, equal to the most recently operational plant, which is generally the largest built. Process information was obtained from published sources in all cases, either patents or other available literature. Because much work is required for commercialization of the furfural-based processes, the economic analyses were adjusted to the year 1995. Moderate rates of inflation were assumed for construction costs as well as for the cost of crude oil, but the real price of crude oil was assumed not to increase. A more detailed discussion of the economic assumptions is presented in Appendix A (Section A.4).

The process studies by ETA yielded for each of the five pairs of alternatives (i.e., chemical production from hydrocarbon versus furfural bases) a discussion of the process chemistry, a process description, a process flow diagram, and an economic summary (Tables A-6 through A-16) consisting of the following elements:

- Plant capacity and location
- Year of costs used and stream factor
- Production costs, including use factors and unit costs:
  - Raw materials
  - Utilities
  - Operating costs
  - Overhead expenses
- Depreciation
- Sales price for 15% DCF return

Results are sufficiently good to establish a value for furfural as a raw material that yields approximately equal profitability for the hydrocarbon and furfural process routes to each product. This value represents both the maximum cost that producers of the furfural derivative can afford to pay in order to recover their capital, as well as the credit the ethanol and furfural producer can expect to receive. These economic results are adequate for broad comparisons. Establishment of more definitive data for the individual furfural process cases was beyond the scope of the work and can be done only after considerably more research, development, and engineering have been completed. The complete text of the ETA study, including flow diagrams and economic summaries, is included in Appendix A.

3.5 RESULTS OF PROCESS STUDIES

In this section the results of the ETA process engineering studies are presented, and their relevance to our report objectives is analyzed. For each of the five chemicals examined, the capital and operating costs for both the hydrocarbon and furfural-based processes are presented as tables to permit all cost components of the competing processes to be directly compared. The tables are condensed from the fully detailed ETA tables in Appendix A. The calculated hydrocarbon-route product sales price for 15% DCF return was assumed to be the same for the furfural-route facilities. Using this value and the capital investment estimates, made as extensions of the known hydrocarbon-route investments, a net raw materials cost for the furfural route was calculated. This cost was then further broken down to the equivalent furan/tetrahydrofuran costs for equal profitability of the hydrocarbon and furfural process routes; the results are shown as footnotes. In addition, process flow diagrams are included for promising furfural-based processes to allow specific review.

3.5.1 Differential Economics for n-Butanol

Table 3-1 compares the economics of n-butanol production via the conventional carbonylation of propylene (the oxo process) and via the proposed furan hydrogenation process. A plant capacity of 200 x 10^6 lb/yr was chosen as representative of current practice. The investment cost for the oxo plant (basis: 1995, U.S. Gulf Coast) is $150 million; within the tolerance of the analysis, the investment for the furan route is the same. Working capital requirements for both processes are in the $15 million range (refer to Appendix A, Section A.4).

With a furan value of $0.25/lb (a 1982 furfural value of $0.08/lb), the production cost and selling price of butanol are identical for both processes. Even with a 310 x 10^6 lb annual feedstock requirement, the net raw materials cost is actually lower for the furan route. The conversion of furan into butanol, as shown in Figure 3-1, appears promising.

Table 3-1. Cost Comparison for n-Butanol
Basis: 1995 dollars; 200 x 10^6 lb/yr plant capacities;
U.S. Gulf Coast location

	Hydrocarbon Route from Propylene	Furfural Route from Furan
Capital Cost Summary ($\$10^6$)		
Battery limits	100	90
Offsites	50	45
Total fixed investment	150	135
Working capital	13.82	15.30
Production Cost Summary ($/unit output)		
Net raw materials	0.43[a]	0.31[a,b]
Total utilities	0.01	0.17
Total operating cost	0.04	0.03
Total overhead	0.04	0.03
Total cost of production	0.52	0.54
Total Cost + Depreciation	0.67	0.68
Selling Price (at 15% DCF)	0.88	0.88

[a] Adjusted for rounding error.

[b] Back-calculated assuming DCF selling price equal to hydrocarbon route.

Equivalent to furan at $0.25/lb.

Equivalent furfural values: 1995, $0.18/lb; 1982, $0.08/lb.

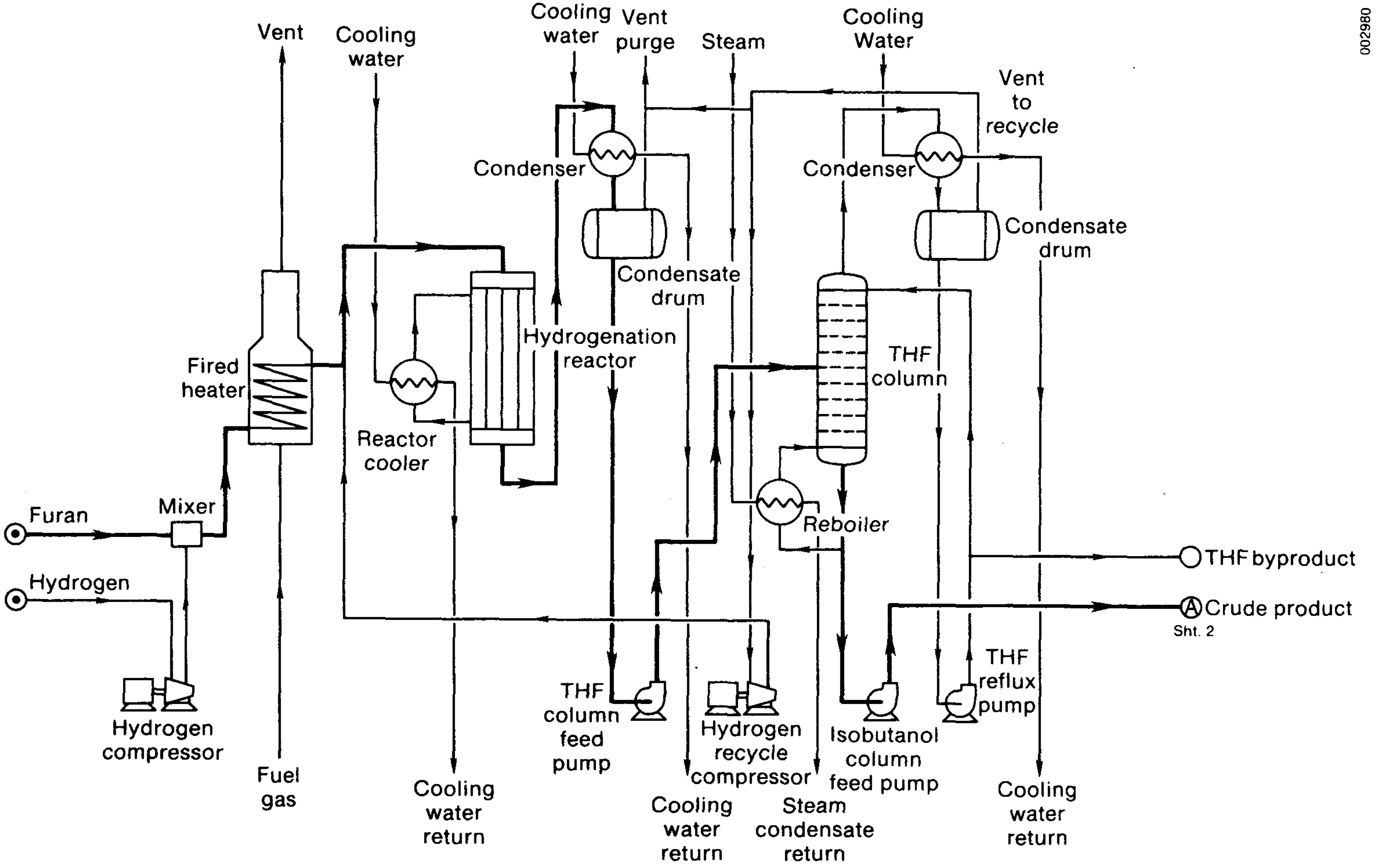


Figure 3-1 (a). **Process Flow Diagram for Production of n-Butanol from Furan** (sheet 1 of 2)

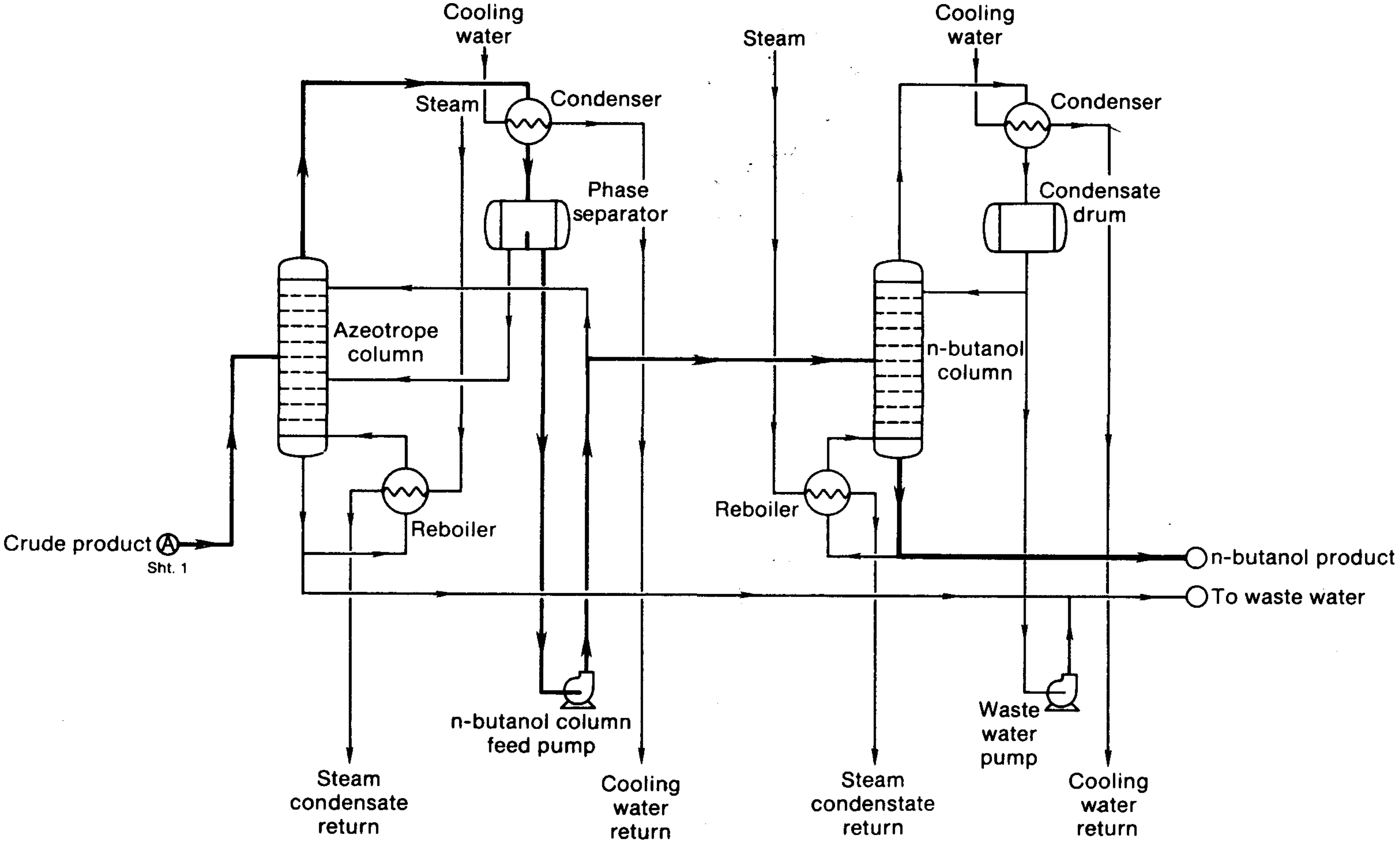


Figure 3-1 (b). **Process Flow Diagram for Production of n-Butanol from Furan** (sheet 2 of 2)

3.5.2 Differential Economics for Butadiene

Table 3-2 summarizes the capital and production costs for butadiene via dehydration/dehydrogenation of tetrahydrofuran. It is clear that even as the cost of tetrahydrofuran is decreased to zero, the THF route can never be competitive under assumed prices with conventional butadiene recovery from the by-product streams of an olefin plant. If the feedstock cost is zero, the selling price required for 15% DCF return is $0.76/lb in 1995.

The estimated market value of butadiene will be at most $0.80/lb in 1995. Since 1.4 lb of THF are required to produce 1 lb of butadiene, any THF value above zero greatly increases the cost of raw materials and all related components. It is improbable that this process would ever be a viable way to upgrade by-product furfural.

Table 3-2. Cost Comparison for Butadiene
Basis: 1995 dollars; 500 x 10^6 lb/yr plant capacities;
U.S. Gulf Coast location

	Hydrocarbon Route[a]	Furfural Route from Tetrahydrofuran		
Capital Cost Summary ($$10^6$)				
Battery limits	—	180	180	180
Offsites	—	90	90	90
Total Fixed Investment	—	270	270	270
Working capital	—	94.06	57.04	36.85
Production Cost Summary ($/unit output)				
Net raw materials	—	1.21[b,c]	0.44[b,d]	0.02[b,e]
Total utilities[f]	—	0.08	0.08	0.08
Total operating cost	—	0.17	0.17	0.17
Total overhead	—	0.18	0.18	0.18
Total cost of production	—	1.64	0.87	0.45
Total Cost + Depreciation	—	1.75	0.98	0.56
Selling Price (at 15% DCF)	0.80	2.12	1.24	0.76

[a] Butadiene coproduced from cracking of hydrocarbon feedstocks.
[b] Back-calculated assuming DCF selling price equal to hydrocarbon route.
[c] Based on THF at $0.85/lb. Equivalent furfural values: 1995, $0.64/lb; 1982, $0.29/lb.
[d] Based on THF at $0.30/lb. Equivalent furfural values: 1995, $0.23/lb; 1982, $0.10/lb.
[e] Based on THF at $0.00/lb. Equivalent furfural values: 1995, $0.00/lb; 1982, $0.00/lb.
[f] Adjusted for rounding error.

3.5.3 Differential Economics for Styrene

The capital and operating costs for production of styrene via benzene alkylation/ethylbenzene dehydrogenation and via butadiene dimerization are shown in Table 3-3. The furfural route is based on butadiene produced from zero-value furfural. The annual capacity for both plants is 10^9 lb. The total fixed investment in 1995 is estimated at over $300 million for both. For the benzene-based process, the net cost of production is $0.58/lb, with the required 1995 selling price of $0.78/lb. The required working capital of $123 million/yr for the butadiene dimerization process is almost twice as high as for the benzene process. Primarily because the feed requirement is almost 1.3 x 10^9 lb of butadiene, the production cost and selling price of styrene from the dimerization process are significantly higher than those for the benzene process.

Table 3-3. Cost Comparison for Styrene
Basis: 1995 dollars; 1 x 10^9 lb/yr plant capacities;
U.S. Gulf Coast location

	Hydrocarbon Route from Benzene	Furfural Route from Butadiene
Capital Cost Summary ($ 10^6)		
Battery limits	215	240
Offsites	90	75
Total fixed investment	305	315
Working capital	62.25	123.37
Production Cost Summary ($/unit output)		
Net raw materials	0.53	0.96[a,b]
Total utilities	0.03	0.10
Total operating cost	0.01	0.02
Total overhead	0.01	0.02
Total cost of production	0.58	1.10
Total Cost + Depreciation	0.65	1.16
Selling Price (at 15% DCF)	0.78	1.37

[a] Adjusted for rounding error.
[b] Back-calculated assuming DCF selling price equal to hydrocarbon route. Based on butadiene at $0.76/lb. Equivalent furfural value: 1995, $0.00/lb.

3.5.4 Differential Economics for Adipic Acid

Process economics for the production of 200 x 10^6 lb/yr of adipic acid from cyclohexane oxidation and tetrahydrofuran oxidation are summarized in Table 3-4. The estimated investment cost for the THF route is $130 million, about 27% lower than the cost of the cyclohexane process of $165 million. One reason is that the THF process is based on conventional oxo technology (see the description of the production of butanol from propylene in Section A.2.1 of Appendix A). The lower investment cost means that, even though the raw materials costs are higher, the working capital, total production cost, and selling price for the THF-derived adipic acid are the same as for the cyclohexane-derived product. This analysis is based on a 1995 value of \$0.85/lb for THF (a 1982 furfural value of \$0.29/lb). Adipic acid from THF does offer substantial promise for future development (Figure 3-2).

Table 3-4. Cost Comparison for Adipic Acid
Basis: 1995 dollars; 200 x 10^6 lb/yr plant capacities; U.S. Gulf Coast location

	Hydrocarbon Route from Cyclohexane	Furfural Route from Tetrahydrofuran
Capital Cost Summary (\$ 10^6)		
Battery limits	110	75
Offsites	55	55
Total fixed investment	165	130
Working capital	18.88	18.36
Production Cost Summary (\$/unit output)		
Net raw materials	0.48	0.59[a,b]
Total utilities	0.12	0.11
Total operating cost	0.04	0.03
Total overhead	0.05	0.03
Total cost of production	0.69	0.76
Total Cost + Depreciation	0.86	0.89
Selling Price (at 15% DCF)	1.12	1.11

[a] Adjusted for rounding error.
[b] Back-calculated assuming DCF selling price equal to hydrocarbon route. Based on THF at \$0.85/lb. Equivalent furfural values: 1995, \$0.64/lb; 1982, \$0.29/lb.

3.5.5 Differential Economics for Maleic Anhydride

Table 3-5 compares the economics for the production of maleic anhydride via butane oxidation and via furan oxidation. Investment cost for a 60 x 10^6 lb/yr plant in 1995 using either process is estimated at \$155 million. The working capital requirements are only about \$7 million/yr. There are only minor differences in the front-end processing, which justifies the assumption that the two plants should cost the same.

At a furan value of \$0.30/lb (a 1982 furfural value of \$0.10/lb), the raw materials costs and the production costs compare favorably with the butane process. Furan-derived maleic anhydride could be sold at \$1.71/lb, compared with \$1.74 for the butane-derived product. The conversion of furan to maleic anhydride is shown in Figure 3-3.

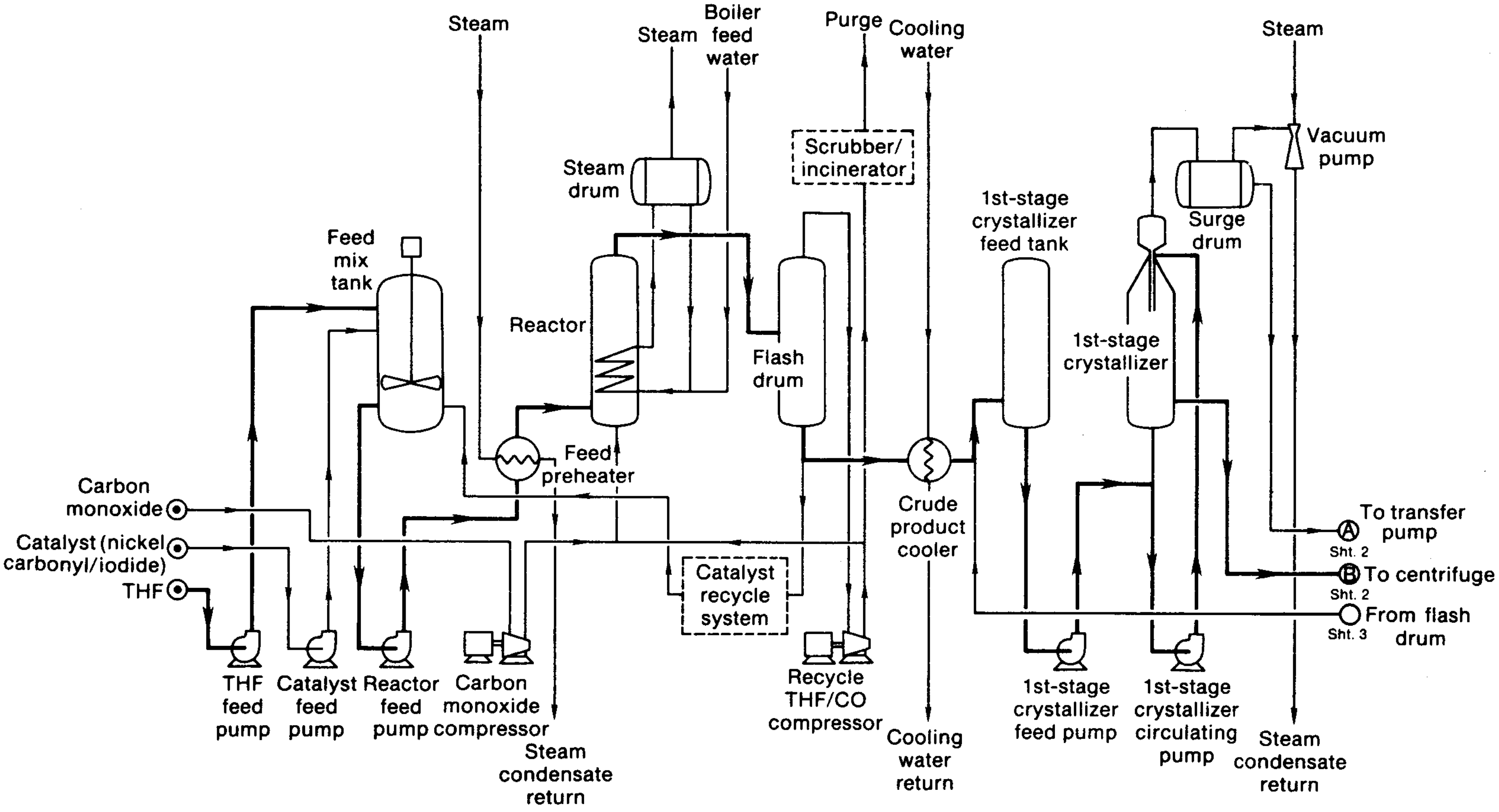


Figure 3-2 (a). **Process Flow Diagram for Production of Adipic Acid from Tetrahydrofuran** (sheet 1 of 3)

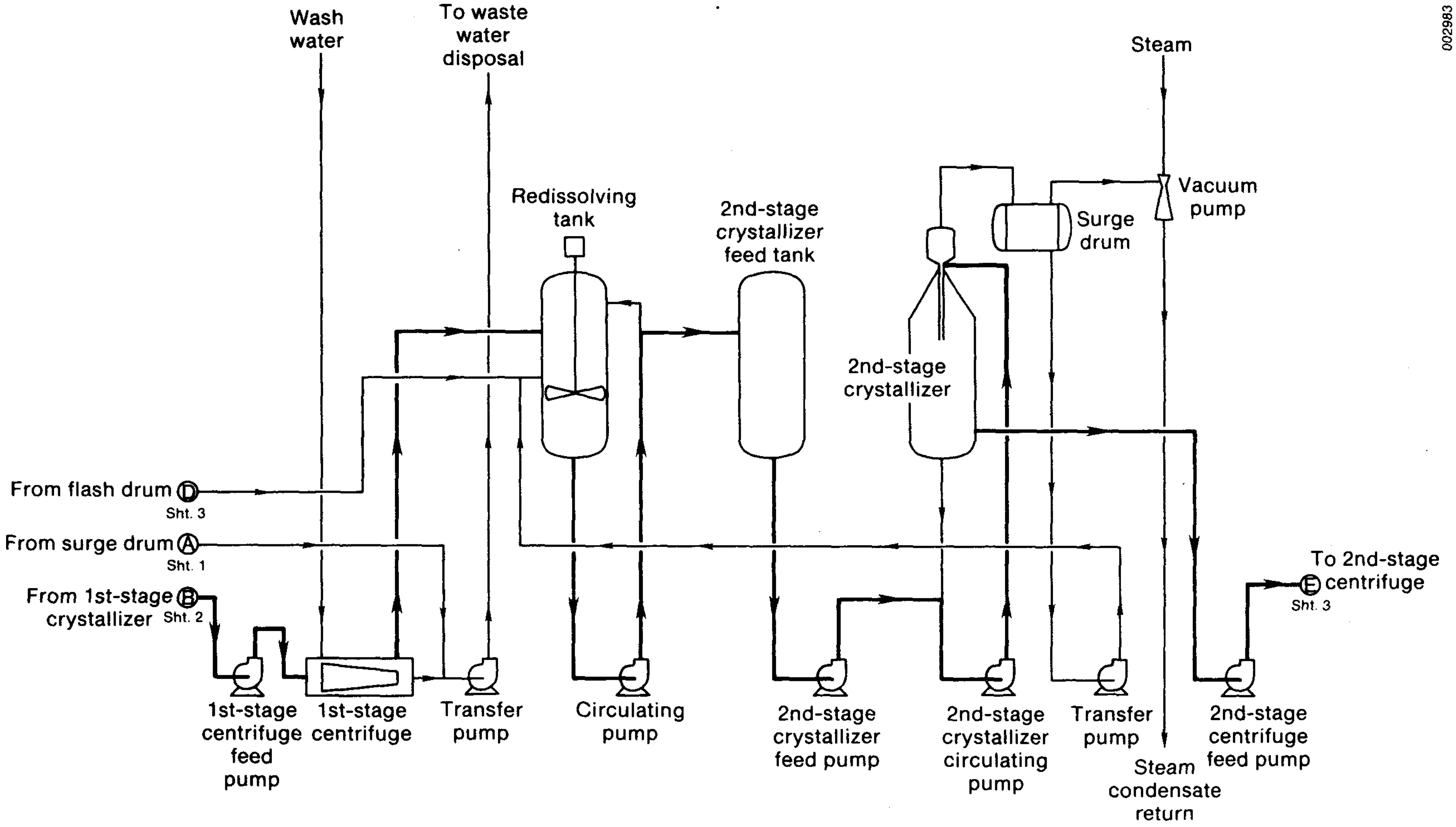


Figure 3-2 (b). **Process Flow Diagram for Production of Adipic Acid from Tetrahydrofuran** (sheet 2 of 3)

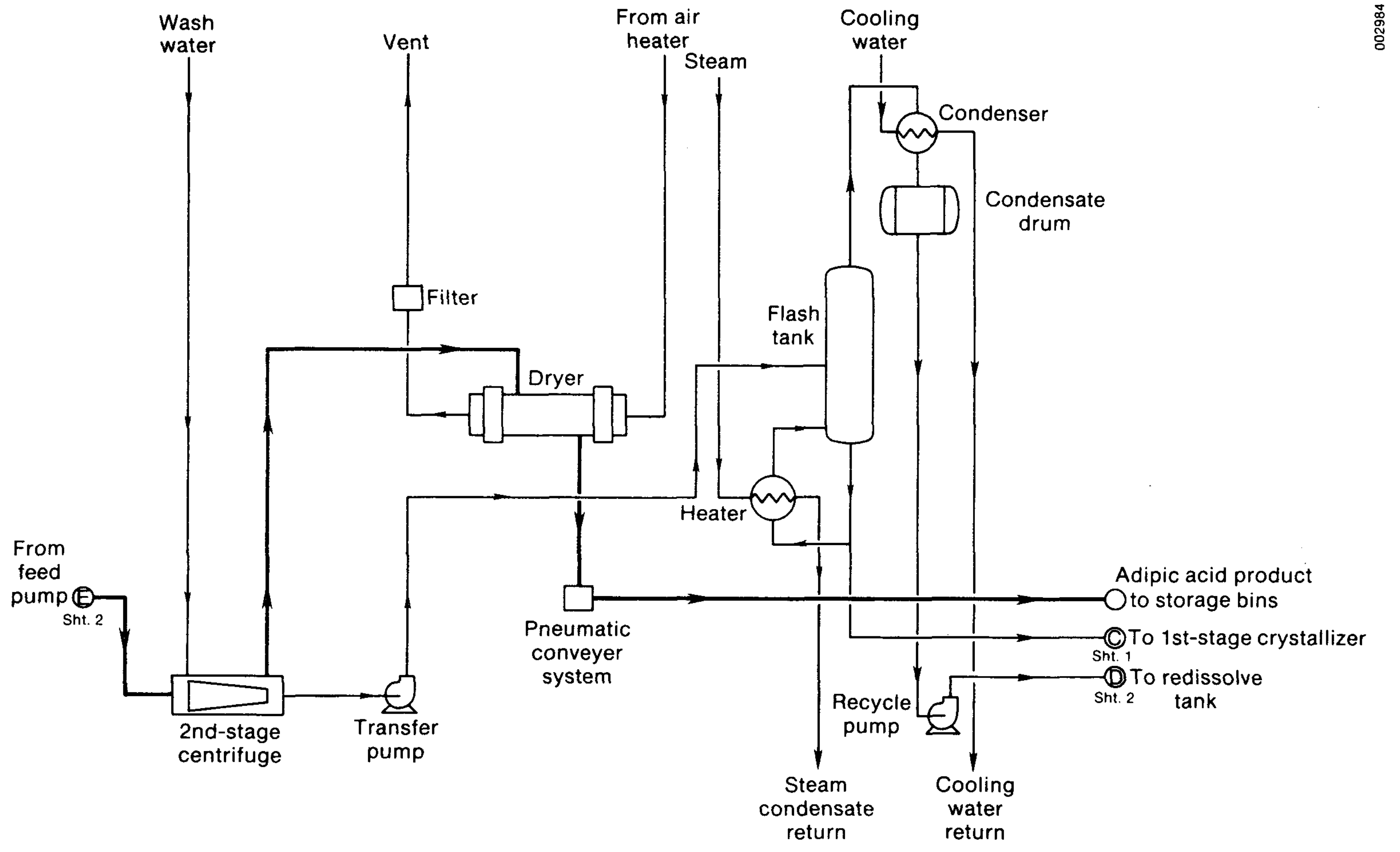


Figure 3-2 (c). **Process Flow Diagram for Production of Adipic Acid from Tetrahydrofuran** (sheet 3 of 3)

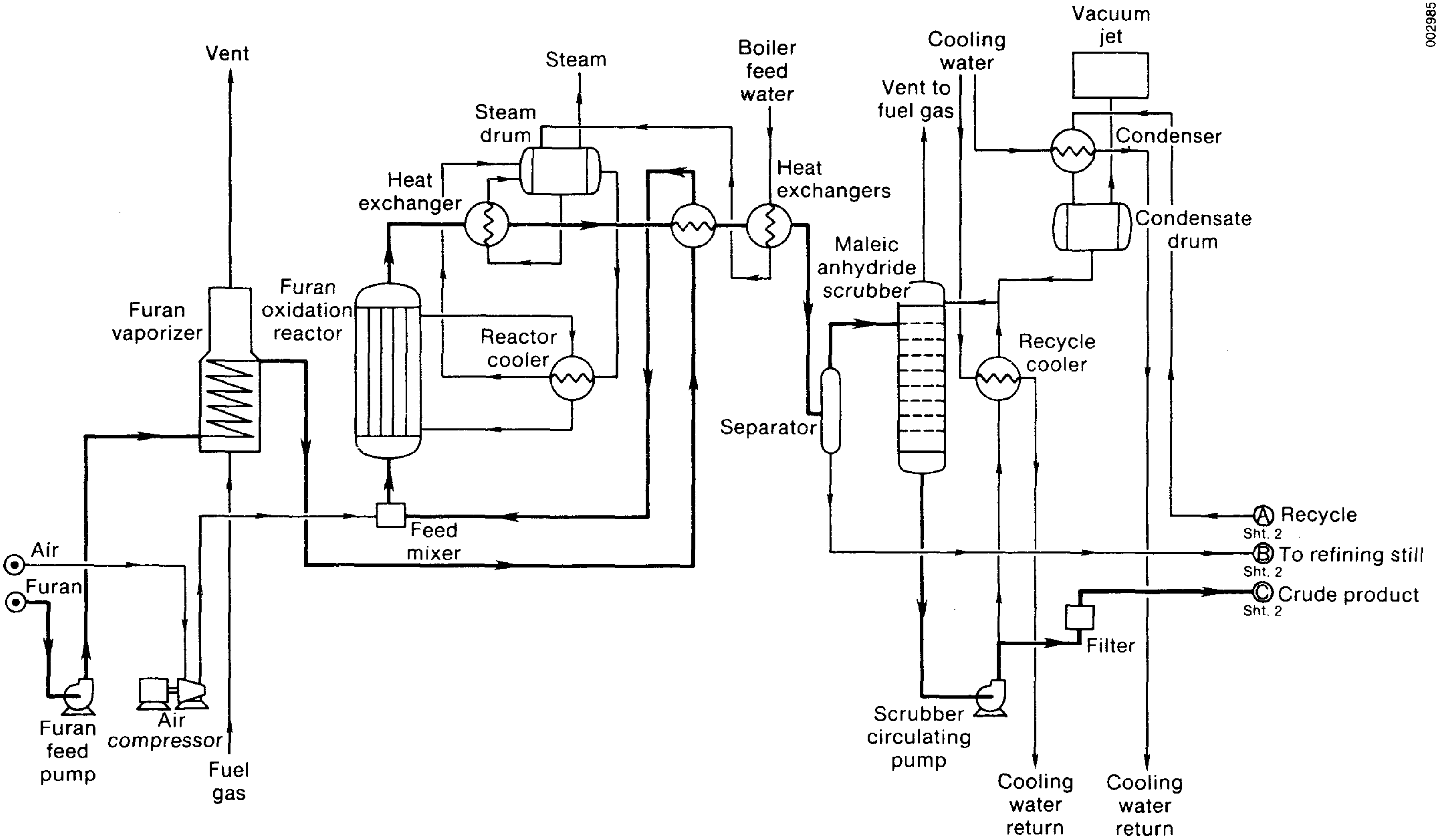


Figure 3-3 (a). **Process Flow Diagram for Production of Maleic Anhydride from Furan** (sheet 1 of 2)

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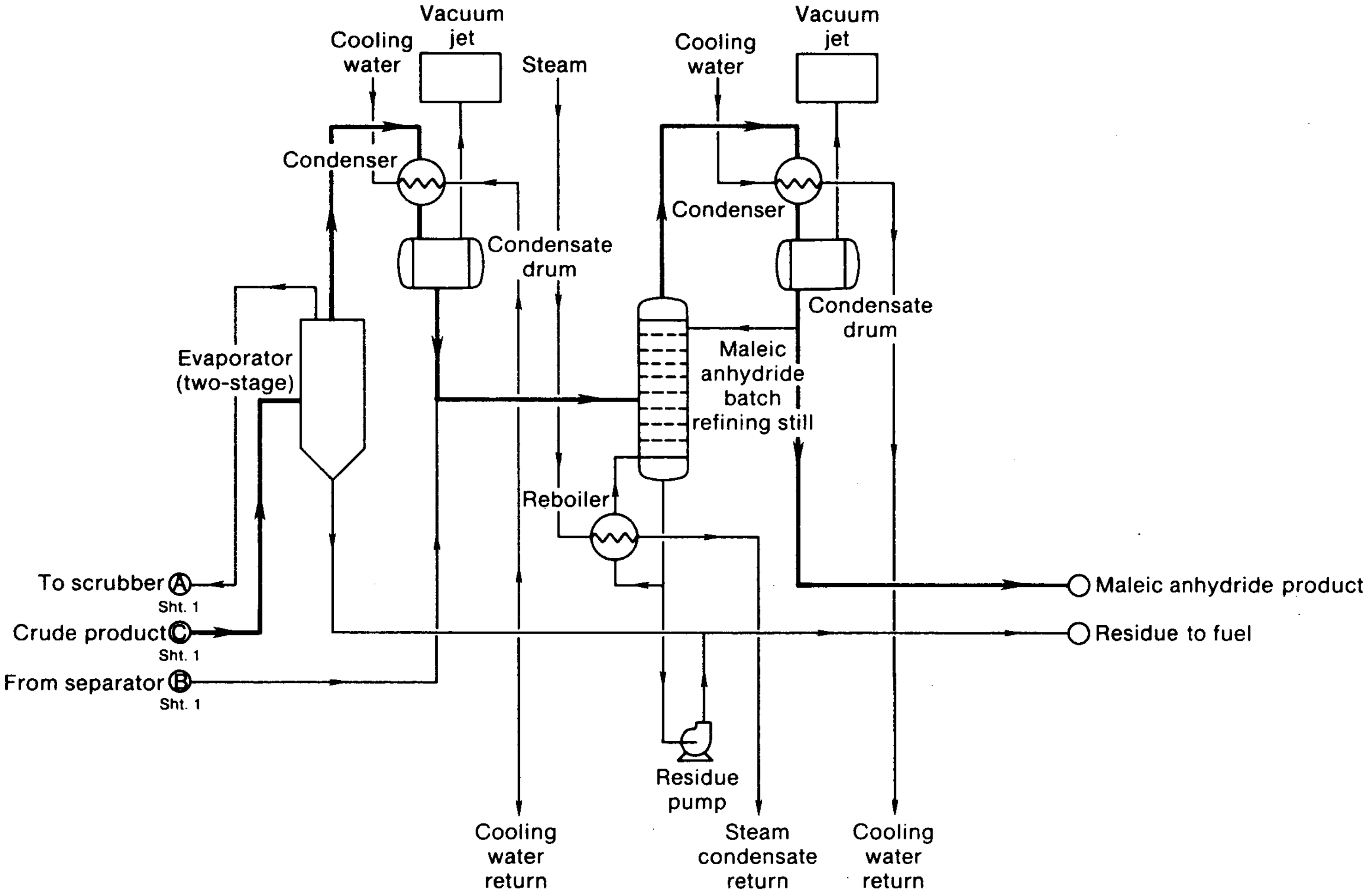


Figure 3-3 (b). **Process Flow Diagram for Production of Maleic Anhydride from Furan** (sheet 2 of 2)

Table 3-5. **Cost Comparison for Maleic Anhydride**
Basis: 1995 dollars; 60 x 10^6 lb/yr plant capacities; U.S. Gulf Coast location

	Hydrocarbon Route from n-Butane	Furfural Route from Furan	
Capital Cost Summary ($ 10^6)			
Battery limits	105	105	105
Offsites	50	50	50
Total fixed investment	155	155	155
Working capital	7.62	7.12	7.44
Production Cost Summary ($/unit output)			
Net raw materials	0.42	0.33[a,b]	0.39[a,c]
Total utilities	0.00	0.01	0.01
Total operating cost	0.12	0.12	0.12
Total overhead	0.12	0.12	0.11[d]
Total cost of production	0.66	0.58	0.63
Total Cost + Depreciation	1.18	1.09	1.15
Selling Price (at 15% DCF)	1.74	1.64	1.71

[a] Back-calculated assuming DCF selling price equal to hydrocarbon route.
[b] Based on furan at $0.25/lb. Equivalent furfural values: 1995, $0.19/lb; 1982, $0.08/lb.
[c] Based on furan at $0.30/lb. Equivalent furfural values: 1995, $0.21/lb; 1982, $0.10/lb.
[d] Adjusted for rounding error.

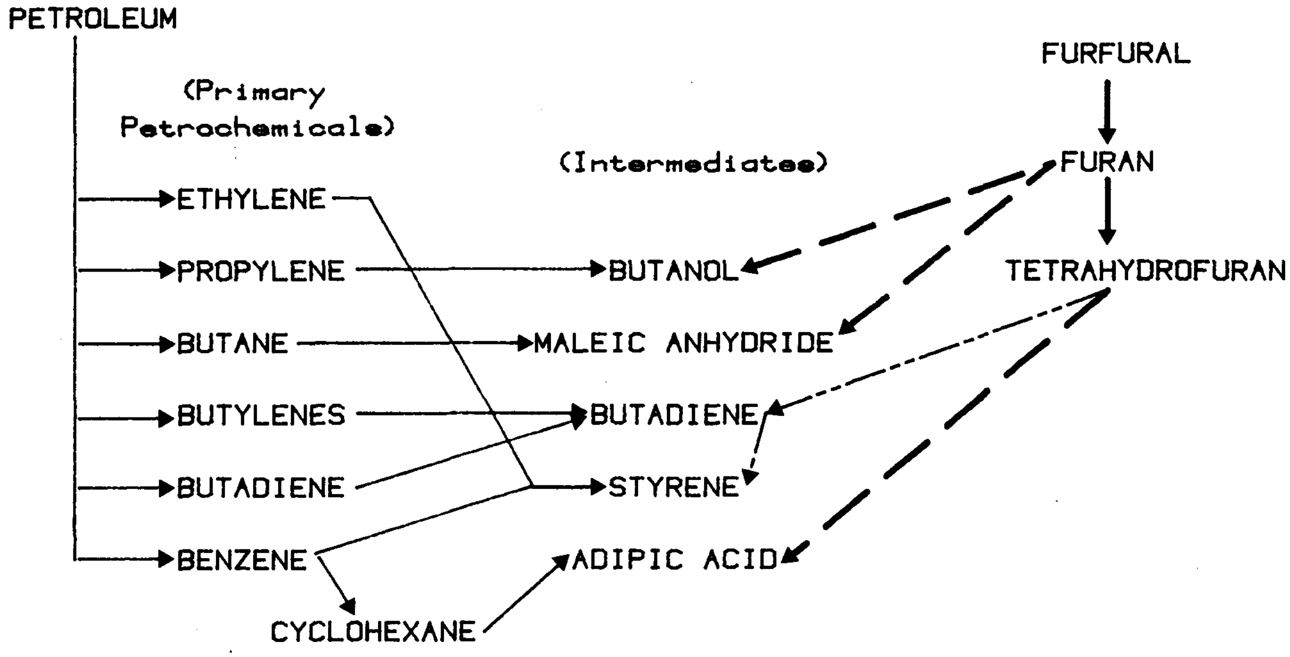
3.5.6 Summary of Results

The results of the process engineering studies performed by Energy Technology Associates indicate that three of the five furfural-based process routes could, with further research and development, compete commercially with existing hydrocarbon-based routes (see Figure 3-4).

The estimated 1982 and 1995 breakeven furfural values that could be credited to a cellulose hydrolysis ethanol operation are shown below in parentheses for each process.

- Furan hydrogenation to n-butanol (furfural, 1982: $0.08/lb; 1995: $0.18/lb)
- Furan oxidation to maleic anhydride (furfural, 1982: $0.29/lb; 1995: $0.64/lb)
- Tetrohydrofuran carbonation to adipic acid (furfural, 1982: $0.10/lb; 1995: $0.21/lb).

If a marginal 1982 furfural value of $0.08 lb is assumed, the adipic acid process shows the greatest promise, followed by maleic anhydride and n-butanol. However, considering the



Existing Petrochemical Routes ————————

Promising "New" (Furfural-based) Routes — — — —

Routes which are not promising - - - - - - - - - - -

Figure 3-4. Summary of Results of Process Studies

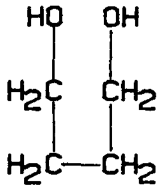
accuracy of the estimates and calculations, all three processes are viable candidates for additional study.

The other two routes, tetrahydrofuran to butadiene and butadiene to styrene, do not have promising commercial potential, chiefly because the raw material costs for those routes are too high.

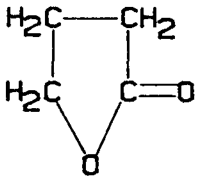
The combined 1982 production of n-butanol, adipic acid, and maleic anhydride was approximately 2.3 x 10^9 lb, indicating vast markets, up to 3.3 x 10^9 lb, potentially available to acid hydrolysis-derived furfural. However, as is examined in Section 4.0, complex factors are associated with the structure of the petrochemical industry that can restrict or augment the extent to which the switching from hydrocarbon- to furfural-based routes would probably occur.

Other potential opportunities for upgrading furfural have been known for many years and have been studied by the paper industry, the German chemical industry, and the petrochemical industry. Some examples include:

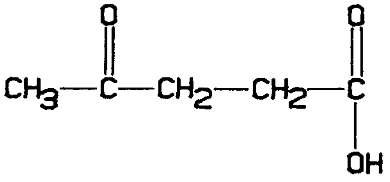
- 1,4-butanediol via THF—a plasticizer and resin intermediate.
- γ-butyrolactone via THF—typical applications are, among others, as a precursor of synthetic blood plasma and of nylon 4.
- Synthetic lubricants—polymers of furfural and furan. Materials for specific military applications were developed in Germany in the 1930s.
- Levulinic acid from furfural alcohol or HMF—polymer and pharmaceuticals intermediate. A large family of derivatives has been developed in extensive work dating back at least 30 years.
- Polyester intermediates—the alcohol and acid analogs of furfural made by hydrogenation/oxidation.
- Thermal decomposition of HMF to furfural and formaldehyde.



1, 4-BUTANEDIOL



γ-BUTYROLACTONE



LEVULINIC ACID

None of this work is new, but all of it could provide starting points for continuing investigation of the furfural market potential.

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SECTION 4.0

IMPLICATIONS OF AN EXPANDED FURFURAL MARKET FOR THE FUELS AND PETROCHEMICAL INDUSTRY

4.1 INTRODUCTION

The work of Section 3.0 establishes an initial estimate of the potential demand for furfural as a chemical precursor. This demand information is presented in Table 4-1. The price column contains the prices that make the furfural process design competitive with the conventional process. The quantities of furfural are the furfural requirements necessary to fill the 1982 demands for the given chemicals.

Table 4-1. Potential Furfural Demand

Market	Price (\$/lb)	Quantity (10^6 lb)
Furfural	\$0.50[a]	140
Adipic acid	\$0.29	1002
Maleic anhydride	\$0.10	454
Butanol	\$0.08	1758

[a] This is a very conservative assumption since, at the current price of \$0.66/lb, profit margins are extremely low.

Although this work is necessary, the breakeven process designs are not sufficient to ensure that firms will adopt the furfural-based processes. This section discusses the additional factors relevant to a firm's decision to switch to a new process. Also, furfural is being considered as a means for lowering ethanol selling prices; this section extends the analysis to the level of the petrochemical industry to view the potential supply of ethanol from lignocellulosic feedstocks and determine the impact of a credit earned from the sale of furfural.

Section 4.2 discusses the qualifications that must be attached to the furfural prices in Table 4-1 and the response of multiproduct firms to changing demands for their products. Chemical plants and petroleum refineries might encounter reduced demand for some of their products as a result of the introduction of furfural derived from acid hydrolysis of cellulose. The interdependency of chemical plants and oil refineries is a result of past periods of cheap oil, which caused petroleum products and natural gas to replace lignocellulosic materials as the raw materials used by chemical plants (Johnson et al. 1983; Flaim et al. 1981; Technical Insights 1980). The relationship is complex because chemical plants can employ a wide slate of petroleum products as feedstocks, and they produce many marketable coproducts from any one production process (Rudd et al. 1981). Analysis of alternative routes to one product does not represent the entire perspective of a plant or the possible effects on the supply of and demand for other feedstocks and products of the plant.

Section 4.3 describes the modeling technique used to further analyze petrochemical substitution possibilities. The model is called PETNET and is a member of the class of models known as generalized network models. Although this model does not provide the user with unambiguous conclusions, its flexibility and computational efficiency allow inferences to be drawn about market and firm behavior for different scenarios and to address a number of alternatives relevant to assessing the status of renewable fuel and chemical technologies.

Assumed constant throughout the various experiments reported in Section 4.3 are the cellulose yield from the various feedstocks and the contribution made by the revenues from the sale of furfural to reduced ethanol costs. It is assumed that a 50% cellulose yield is the maximum practical level attainable (Wright 1983). This percentage determines the yield of ethanol per unit of feedstock, and although it should not be regarded as an absolute constant, increases will come only as a result of substanital R&D.

The impact of a positive price for furfural on the selling price of ethanol has been based on two important assumptions. First, it is assumed that furfural is supplied in sufficient quantities to fill the final demands for furfural and the three chemicals identified in Section 3.0, and that competition drives the price of furfural down to its lowest value in use ($0.08/lb). This is equivalent to assuming that the furfural market can not be segmented to allow different prices to exist simultaneously. The second assumption pertains to the link between revenues derived from the sale of furfural and the resulting decrease in ethanol selling prices. Since ethanol and furfural are coproduced from the acid hydrolysis of cellulose, the burden of covering capital and operating costs and rate of return are shared between the two products. Any revenue generated in excess of recovery costs from the sale of furfural decreases the burden placed on ethanol prices. If this decreased burden is translated into lower selling prices for ethanol, the competitive status of ethanol as an octane enhancer or neat fuel is improved.

Furfural recovery costs are known to be positive but accurate estimates are not available. The true costs will only be known when the plant design is optimized for the coproduction of ethanol and furfural instead of regarding furfural as a waste product and optimizing ethanol production alone. Given this lack of information, recovery costs are assumed to be zero and the full revenue of $0.08/lb is applied to lowering the ethanol selling price by $0.28/gal (based on a yield of 3.5 lb furfural/gal ethanol).

4.2 THE STRUCTURE AND BEHAVIOR OF PETROCHEMICAL MARKETS

4.2.1 Industry Structure and Prices

Because chemical plants and oil refineries produce a fixed slate of products from various feedstocks, the price of any one product is not determined in isolation. The selling prices of the slate of products are jointly determined to best meet management objectives for the plant as a whole. Any one price must be considered in a larger integrated-market context: changes in the market may imply changes in the price of one product, which in turn may cause changes in related product prices.

A firm's reaction to increased competition for one of its products will be governed by the technology flexibility, the marginal cost of production, and the overhead costs to be shared by all the products sold by the firm. If other coproduct prices can be increased to cover overhead and a targeted rate of return, the firm can react to increased competition in one market by lowering its price to a point where marginal cost is just covered. In cases of coproduction, the secondary products are effectively (in an accounting sense) produced at no cost to the firm, and severe price competition could drive the price below the marginal production cost or so low that total revenues (from all products) decline. Such price adjustments of products can be expected to persist until competition in one market or in several markets increases sufficiently to require an adjustment of the amount or type of feedstock or the conversion process used by the plant. If an accurate picture of the potential of new processes and products is to be obtained, these price, quantity, and process adjustments must be taken into consideration.

4.2.2 Chemical Plant Structure and Behavior

There are three general types of petrochemical precursors: olefins, aromatics, and paraffins. Of these three, olefins constitute the largest group, their manufacture requiring approximately 50% of the total energy consumed in the production of petrochemicals (Gaines et al. 1980). The olefin compounds are ethylene, propylene, and butadiene, with ethylene accounting for half of the total olefin production (Gaines et al. 1980). The primary sources of ethylene are ethane, naphtha, gas oil, propane, and butane. Propylene and butadiene are coproduced with ethylene and are therefore derived from the same feedstocks. As a first approximation, therefore, the olefin portion of the petrochemical industry can be represented by ethylene-producing plants.

The PETNET model represents the olefin portion of the petrochemical industry by processing data for existing U.S. ethylene plants (Farina 1982; Gaines et al. 1980). PETNET in its current form does not cover the paraffin or aromatic portions of the petrochemical industry and thus does not represent the full slate of chemicals derived from petroleum and natural gas products. However, focus on the olefin portion of the petrochemical industry sufficiently represents the effects of furfural substitution in various scenarios. In this section we adopt the perspective of the olefin plant and use the engineering data to make conclusions about the market implications of a competing furfural technology.

Furfural-based technology could compete with conventional technology in two ways: new companies could be formed utilizing the new techniques to compete against existing firms, or the new technology could be adopted as an alternative to the conventional route by the existing firms. Since these chemicals are conventionally manufactured from coproducts of ethylene production, utilization of furfural as a feedstock will most likely depend on the choice made by the plant manager between the competing technologies. If a chemical producer regards the conventional precursor as an effectively free coproduct, the prices might be allowed to fall close to zero to compete with an alternate, furfural-based route. As a result, the competition between the existing plant and a new market entrant might be so severe that the only way the new technology might be successful would be through adoption by the existing plant. This is due to the fact that without the benefits of coproduct revenues, the single-product technology could not compete. We therefore examine the factors affecting a firm's decision to switch from an existing technology to an alternative.

The engineering data provide a first approximation of the cost goal for the new technology by developing a process design that allows a chemical to be produced from furfural at a price just competitive with the conventional process. A technology that cannot meet this first cost goal is unlikely to be given any consideration by industry. However, meeting this cost goal can only create interest on the part of industry. The decision to adopt the technology will be based on additional plant-specific information. The capital equipment for the conventional process is in place and, at best, a new process capable of generating a rate return equal to that of the old process (the case where the cost goal is just met) is regarded as an equivalent investment. In this case, the direct costs of switching processes and the time involved may induce the firm to continue the conventional process. That is, equivalence of cost between the new and conventional technology may not be sufficient to induce adoption since switching costs would be incurred to earn an equivalent return.

A more challenging but more effective cost goal is to achieve through R&D a selling price for the product from the new process that is less than the conventional selling price but greater than the production cost of the conventional process (plus depreciation). Within this range the new process offers the firm a rate of return that is more than competitive with the old process. Industry response to a new process that meets this second cost goal is positive, but again timing of the process switch will be governed by the capital structure of a given firm. The age of the existing capital equipment and the financial and accounting conventions used by the firm in valuing assets and depreciating capital will determine when the firm will decide to switch to a new process. In general, the older the existing capital equipment, the sooner the new process will be adopted. However, unless firms in the industry are identical in the vintage of their capital, response to the price of the alternative will not be uniform and total conversion to the new process will take time. For example, naphtha-based ethylene plants offer advantages over plants using other feedstocks, but naphtha-based plants coexist with these other plants.

To meet the third cost goal, the new process must be capable of offering a fully loaded price that is less than or equal to the operating expenses alone of the conventional technology. In this case, there is incentive to dispose of the existing equipment and immediately incorporate the new process. In this case, however, the firm is faced with the delay involved in making the new process fully operational, and this time factor will determine when the conventional process can be completely discontinued.

The above discussion does not strictly apply to multiproduct firms. Such a firm is interested in a technological configuration that offers the strongest overall financial position. For a new technology to be considered by a firm, it must have a positive net effect. A new process capable of improving one or two product lines while weakening the competitive position of the remaining products will not be a strong candidate for consideration. Conversely, a technology that substitutes completely and still allows the firm to remain productive and competitive will be viewed more favorably, since the overall financial position of the firm has improved.

4.2.3 Oil Refinery Structure and Behavior

This section discusses the effects of the competition between conventional and furfural-based processes on oil refineries, which supply most of the feedstocks for the conventional routes.

Refineries maximize their revenue by attempting to derive the optimal mix of products from the barrels of crude oil processed. The refinery can vary the type of crude oil processed or the secondary processing steps as the demands for fuels and chemicals vary. From any given configuration of type of crude oil and processing steps, the refinery produces a fixed slate of several products. The best-known example of refinery adjustment in response to changing demand is the seasonal swing between cracking heavy residual oil for enhanced gas production in summer and using the residual for heating oil in the winter.

The implications of different furfural scenarios for refineries will depend on the extent to which the new technology is capable of duplicating the slate of products obtained from the conventional process. The degree to which a chemical plant is capable of meeting its demands with a new technology or mix of technologies will determine whether the firm will reduce its general level of demand for petroleum feedstocks or simply demand less of one specific feedstock and possibly more of another. These situations may not be perceived as fundamentally different by the refinery, since petrochemical demands account for only about 4.5% of total refinery output (Gaines et al. 1980). A change in the mix or total amount of petrochemical feedstocks needed from refineries will only marginally change refinery product prices or processing steps if furfural displaces only small amounts of refinery feedstocks.

Effects on the refinery become more visible and important when the wider scope of the furfural scenario is considered. Furfural is produced in conjunction with the production of ethanol from the acid hydrolysis of cellulosic materials. Ethanol is used both as a blender, reducing gasoline demand, and as a precursor for chemicals, thereby reducing the demand for petrochemical feedstocks. Methanol is also a source of blending components and chemical products and may further reduce the demand for petroleum products. In this wider context, it may be possible to replace almost all the primary products of the refinery. Refineries may respond to these changing demands for their products by altering the mix of secondary processing steps, changing the grade of crude processed, or reducing the number of barrels of oil refined. From an energy conservation perspective, the greatest value is realized if products such as furfural and ethanol reduce the number of barrels refined rather than initiate a readjustment in utilization of refinery products.

4.3 PETNET

The PETNET model (Farina 1982) was designed to represent the existing structure of the U.S. petrochemical markets. PETNET, in conjunction with an optimization computer code, can describe the optimal allocation of resources in the petrochemical industry. In this section we describe the operation and structure of PETNET and discuss the ability of PETNET to predict the response of plants and refineries to some of the situations discussed above.

There are three major components of the PETNET model: final demands, supplies, and arcs or structural relationships that represent conversion processes. An optimal solution of the model is defined as the least-cost method of filling final demands, given the availability of resources and the structural ties linking supplies to demands. The magnitudes of the supplies and demands are fixed for any one simulation but may be varied to best fit a given scenario. The arcs or structural relationships provide a summary of the conversion of supplies to demands, and therefore specify the set of alternative routes that may be utilized to fill demands.

4.3.1 Structure of PETNET

The U.S. petrochemical and fuel industry is represented in the model by demands for 29 chemical and fuel products, which are listed in Table 4-2. Chemical demands represent major products that are inputs to final demand production processes with base-case values representative of 1982 levels of consumption. The fuel demands are also representative of the 1982 market; they include gasoline and the major fuel extenders and octane enhancers. The fuel demands also include ethanol, which is currently derived from starch fermentation processes, and methanol, which is produced from natural gas.

Table 4-2. Base-Case Fuels and Chemicals Final Demands

Fuel/Chemical	Base Case Units (10^6 units)	Demand
Ethylene oxide	pounds	5,512.5
Ethyl acetate	pounds	250.0
Chemical grade ethanol	gallons	200.0
Fuel ethanol	gallons	400.0
Gasoline	gallons	74,800.0
Tertiary butyl alcohol	gallons	100.0
Ethyl benzene	pounds	7,899.4
Ethylene dibromide	pounds	1,000.0
Miscellaneous ethylene	pounds	10.0
Vinyl chloride	pounds	6,819.9
Low density polyethylene	pounds	4,860.0
High density polyethylene	pounds	4,860.0
Methyl tertiary butyl ether	gallons	90.0
Formaldehyde	pounds	2,454.0
Methylamines	pounds	247.9
Celanese fuel methanol	gallons	905.4
Chemical grade methanol	gallons	256.0
Oxinol	gallons	10.0
Fuel methanol (neat)	gallons	50.0
Methyl methacrylate	pounds	1,120.0
Acetic acid	pounds	1,479.6
Acetaldehyde	pounds	562.0
Ethylene dichloride	pounds	1,840.0
Butanol	pounds	823.0
Adipic acid	pounds	1,200.0
Butadiene	pounds	1,830.0
Styrene	pounds	5,870.0
Maleic anhydride	pounds	304.0
Furfural	pounds	140.0

Alternative supplies of feedstocks for producing these final demands include renewables and nonrenewables. Base-case supplies and prices of the nonrenewable feedstocks are presented in Table 4-3 along with approximate 1982 consumption. Refinery product supplies are derived from data on average refinery product fractions from oil distillation. That is, data on average product yields per barrel of oil (American Petroleum Institute 1983) are applied to estimates of oil refined to determine the availability of oil-derived fuel and petrochemical supplies. In addition, natural gas and natural gas product supplies are included to represent the feedstocks available for production of final demand products. The supplies include the "heavy" portions such as distillates and residuals, although in its current configuration the model does not include final demands for products that utilize these feedstocks.

Table 4-3. **Base-Case Nonrenewable Feedstock Supplies and Prices**

Feedstock	Supply Units	Price (10^6 units)	(1982 $/unit)
Gasoline			
Refinery	gallons	79,615	1.00
Imports	gallons	2,792	1.01
Jet fuel			
Refinery	barrels	284	45.15
Imports	barrels	4	45.57
Ethane			
Refinery	pounds	7,825	0.11
Imports	pounds	0	
Kerosene			
Refinery	barrels	52	45.15
Imports	barrels	5	45.57
Distillate			
Refinery	barrels	963	41.87
Imports	barrels	34	42.29
Residual			
Refinery	barrels	516	34.27
Imports	barrels	272	34.69
Naphtha	barrels	346	46.45
Gas oil	barrels	31	42.00
Propane	pounds	4,100	0.115
Butane	pounds	812	0.26
LPG			
Refinery	pounds	16,615	0.15
Imports	pounds	13,828	0.16
Miscellaneous refinery products	barrels	447	20.00
Natural gas	scf	18,000,000	0.003

The base-case supplies and prices for renewable resources are presented in Tables 4-4 and 4-5, respectively. The supplies and prices of the two major categories of renewable feedstocks—corn grain and lignocellulose—are differentiated by ten federal regions so that it is possible to derive information from the model about the optimal feedstock combinations. Moreover, the regional structure makes possible analyses of how a renewable industry might emerge, given the specific feedstocks available and the product demands.

Process routes link the available feedstocks to the exogenous demands. That is, the model seeks to fill (exactly) the expressed final demands by utilizing the available production processes and feedstocks. The optimizing criterion applied in choosing the structure of the industry is cost minimization. Thus, all processes are represented by an

Table 4-4. **Base-Case Supplies of Renewable Lignocellulose and Corn Grain Feedstocks by Region**

Region	Base-Case Feedstock for Acid Hydrolysis					
		Logging Residues[a]				
	Corn Residues (10^6 t)[b]	Softwood (10^6 t)[c]	Hardwood (10^6 t)[c]	Growing Wood (10^6 t)[c,d]	Total Lignocellulose (10^6 t)	Corn Grain (10^6 bu)[e]
I	0	1.734	1.464	49.1	52.298	0
II	0.950	0.253	0.851	22.6	24.654	56.045
III	3.900	0.640	5.731	84.6	94.871	241.976
IV	6.460	5.950	8.726	201.5	222.636	444.260
V	50.550	0.406	2.569	66.7	120.225	3302.790
VI	2.030	2.504	3.015	83.4	90.949	160.818
VII	38.330	0.009	0.558	15.2	54.097	2547.050
VIII	4.260	1.299	0.011	32.5	38.07	275.261
IX	0.530	3.509	0.314	31.4	35.753	41.156
X	0.080	12.323	0.918	102.0	115.321	12.493
Total	107.09	28.627	24.157	689.0	848.874	7081.849

[a] SERI calculations based on data from the following sources: Cost and McClure 1982; Monteith 1981; USDA 1978; USDA 1981; USDA 1982.

[b] Max et al. 1983. Based on 1979 agricultural census data. Green (wet) tons at approximately 30% moisture.

[c] Green tons.

[d] Calculated as 2% of total growing biomass estimated by U.S. Forest Service, USDA (1981).

[e] 1979 agricultural census data at approximately 15% moisture.

Table 4-5. **Base-Case Renewable Lignocellulose and Corn Grain Prices by Region**[a]

Region		Logging Residues			
	Corn Residues ($/t)	Softwood ($/t)	Hardwood ($/t)	Growing Wood ($/t)	Corn Grain ($/bu)
I	NA	24.10	21.39	30.00	3.00
II	25.00	24.10	21.39	30.00	3.00
III	25.00	24.10	21.39	30.00	3.00
IV	30.00	25.41	20.85	30.00	3.00
V	20.00	24.10	21.39	30.00	3.00
VI	40.00	25.41	20.85	30.00	3.00
VII	20.00	24.10	21.39	30.00	3.00
VIII	25.00	21.48	21.79	30.00	3.00
IX	25.00	21.87	22.05	30.00	3.00
X	NA	23.95	29.78	30.00	3.00

Sources: Max et al. (1983) and SERI calculations based on sources listed in footnote a of Table 4-4.

[a] Prices are for green (wet) tons except for corn, which is at 15% moisture.

input-output coefficient or yield of product per unit of feedstock, the unit cost (operations, capital changes, and profit margin), and capacity. In seeking a minimum cost solution to producing final demands, the model considers relative production costs and allocates production according to the least-cost principle, taking constraints on feedstocks or production capacity into account.

A list of conventional process routes included in the model is presented in Table 4-6. To these currently exercised routes several alternative production processes, including the furfural routes identified in Section 3.0, have been added. The major emphasis of this study is ethanol production, so the alternative production processes involve routes to ethanol. Figure 4-1 displays the feedstock/process/product routes for ethanol production currently included in the model. As indicated, given the several feedstocks that can be utilized and the two production routes available, the model includes several diverse options, and each is subject to the regional feedstock price diversity and resource constraints.

Table 4-6. Conventional Petrochemical Process Routes Included in the PETNET Model

Input	Product	Input	Product
Oil	Gasoline		
	Jet fuel	Benzene	Styrene
	Ethane	Butylene	Butadiene
	Kerosene	Propylene	Butanol
	Distillate	Benzene	Adipic acid
	Residual	Butylene	Maleic anhydride
	Naphtha		
	Gas oil	Acetaldehyde	Acetic acid
	Furfural	Acetic acid	Ethyl acetate
Natural gas	Ethene	Methanol	Methyl tertiary butyl ether
	Methanol		
	Propane		Formaldehyde
	Butane		Acetic acid
Ethane	Ethylene	Furfural	Tetrahydrofuran
Propane	Ethylene		
Gas oil	Ethylene		
Butane	Ethylene		
Liquified petroleum gas (LPG)	Ethylene		
Ethylene	Acetaldehyde		
	Ethanol		
	Ethylene oxide		
	Ethyl benzene		
	Ethylene dibromide		
	Vinyl chloride		
	Ethylene dichloride		
	Polyethylene		
	Benzene		
	Propylene		
	Butadiene		
	Butylene		

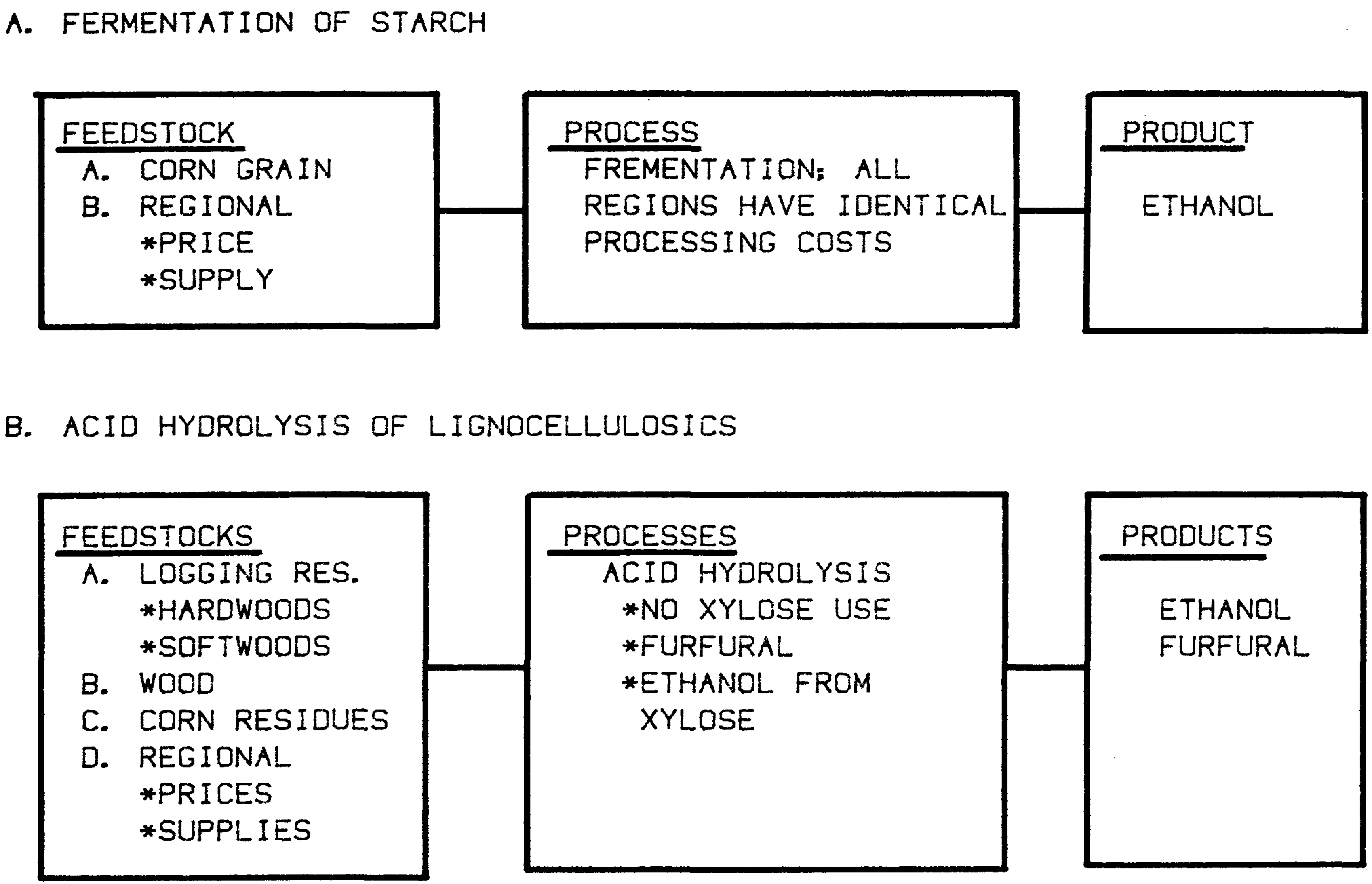

Figure 4-1. Feedstock/Process/Product Routes for Ethanol Production

Given the range of resources available and their respective prices, it is evident that no single process route dominates. Ethanol can be produced in a variety of ways, and the purpose of the modeling effort is to derive the implications of this diversity for ethanol R&D efforts and for the potential for ethanol to play an important role in the fuel and petrochemical sector.

Before turning to an analysis of specific cases, it is instructive to examine the base-case implications of the data. First, because corn prices are not differentiated by region ($3.00/ bu) and because the conversion routes are also undifferentiated (2.5 gal/bu), the cost of ethanol from fermentation of grain is $1.84/gal in the base case ($1.20/gal feedstock cost and $0.64/gal processing cost). Similarly, wood feedstocks, defined as 2% of growing tree stock, are not differentiated by cost ($30/t in all regions) or conversion yield (20 gal/t). Thus, all ethanol from acid hydrolysis of wood costs $2.05/gal ($1.50/gal feedstock cost and $0.55/gal production cost). The lack of good data on the supply functions for these feedstocks requires these ethanol production routes to be uniform over all regions for this exercise. However, the diversity of other lignocellulosic feedstock supplies and prices (Tables 4-4 and 4-5) result in considerable diversity in the implied ethanol production cost. Given the base-case data it is possible to draw conclusions about the order in which the model will fill ethanol demands.

Regional ethanol production costs for acid hydrolysis processes using corn and logging residues (the major residue supplies represented in the model) are listed in Table 4-7. The data indicate the potential for producing a total of almost 4 x 10^9 gal of ethanol at an average price of $1.36/gal, based on current acid hydrolysis technology. Although this price is above that of gasoline ($1.00/gal) it is below that of current ethanol production from fermentatin of corn grain (about $1.70/gal). This suggests that the first penetration of acid hydrolysis ethanol will be the displacement of corn fermentation. That is, new acid hydrolysis capacity will tend to compete with and displace existing capacity before augmenting current supplies. Instead of supplementing ethanol supplies from corn fermentation, acid hydrolysis may result in the displacement of one renewable fuel source with another, resulting in no net reduction of oil use. Additional implications of this phenomena will be addressed later when a structured scenario is applied to the model.

With regard to the potential contribution of the three feedstocks listed in Table 4-7, corn residues provide the largest contribution (2.8 x 10^9 gal, or 72% of the total) at the lowest average price ($1.25/gal). Most of the potential for ethanol from corn residues is in Regions V and VII—the Corn Belt states—which also have the lowest cost sources (based on the estimated cost of residue feedstocks of $20/t, Table 4-5). If ethanol can find extensive markets at about $1.20/gal, it appears that the corn-growing regions could benefit from the success of acid hydrolysis technology. The use of corn residues would enhance agricultural revenues to corn growers and provide locally produced fuels to displace gasoline.

Logging residues offer the opportunity for additional supplies of ethanol but at higher average prices (Table 4-7) that are not substantially lower than current corn grain-based ethanol costs. However, the wide regional availability of these residues suggests that acid hydrolysis ethanol production could become widely dispersed and provide locally produced fuels in regions with low levels of grain production.

Table 4-7. Base-Case Cost for Ethanol Production by Acid Hydrolysis of Lignocellulose Feedstock

Region	Corn Residues		Logging Residues				Regional Weighted Average Price ($/gal)[c]	Total Available Quantity (10^6 gal)
			Hardwood		Softwood			
	Cost[a] ($/gal)	Quantity[b] (10^6 gal)	Cost[a] ($/gal)	Quantity[b] (10^6 gal)	Cost[a] ($/gal)	Quantity[a] (10^6 gal)		
I	—	—	1.62	29.30	1.75	36.40	1.53	65.70
II	1.39	24.70	1.62	17.02	1.75	5.06	1.51	46.78
III	1.38	101.40	1.62	114.60	1.75	12.80	1.52	228.80
IV	1.58	167.96	1.59	174.52	1.82	119.00	1.55	461.48
V	1.19	1313.00	1.62	51.38	1.75	8.12	1.21	1372.50
VI	1.96	52.78	1.59	60.30	1.82	50.08	1.78	163.16
VII	1.19	996.58	1.62	11.16	1.75	.18	1.19	1007.92
VIII	1.38	110.76	1.64	.22	1.62	25.98	1.43	136.96
IX	1.38	13.78	1.65	6.28	1.64	70.18	1.60	90.24
X	—	—	2.04	18.36	1.75	246.46	1.77	264.82
Weighted average cost[d]	1.25	2780.96	1.62	483.14	$1.75	574.26	1.37	3838.36

[a] Cost ($/gal) of producing a gallon of ethanol from acid hydrolysis of the indicated feedstock. The cost includes the specific regional feedstock price, the conversion yield, and the conversion cost.

[b] The maximum quantity of ethanol that can be produced at the indicated cost, given base-case resource supplies.

[c] Weighted (by quantities) average required cost per gallon of ethanol, assuming all feedstocks are fully utilized.

[d] Weighted (by regional quantities producible) average feedstock cost per gallon of ethanol, assuming all regions are at full production.

Finally, the data in Table 4-7 suggest that the regional impacts of a developed acid hydrolysis industry will be largest in Regions V and VII. Given the average price, the industry most likely will first develop and eventually be concentrated in these regions. More in-depth analyses of the resources in these regions are required to further refine these results and to predict the local impacts and economic consequences.

4.3.2 Applications of PETNET

The results of the PETNET model describe the optimal allocation of refinery products, natural gas, and biomass feedstocks in meeting fuel and chemical demands. Because of the promising results of the engineering analyses described in Section 3.0, the furfural routes to butanol, adipic acid, and maleic anhydride have been included in PETNET, allowing the conclusions of Section 3.0 to be extended to the level of the petrochemical industry. Varying the prices of feedstocks and conversion costs of furfural and the conventional routes not only allows the conclusions of the engineering data to be verified but also suggests the reactions of refineries and chemical plants to these changes. PETNET is also capable of predicting the response of the petrochemical markets to the levels of ethanol production from acid hydrolysis corresponding to different levels of furfural production. Finally, by varying the relevant prices and process costs in the model, scenarios relating to the three levels of cost goals discussed above and to technology transfer can be constructed and analyzed.

4.3.2.1 Fixed-Blend Ethanol Demands

To make a first approximation of the potential for ethanol, the model was run with the base-case data but at various levels of ethanol contribution to total transportation fuel demands. All feedstocks and process data are set at their base-case levels. Thus, all ethanol technologies operate at their current technology and cost levels, and no furfural by-product credit is considered. The only change made from case to case is the amount of ethanol for fuel demand. Total transportatioin fuel demand is held constant at 80 x 10^9 gal, and the ethanol contribution is progressively raised from 0.5% to 25% of the total amount. Additionally, for each case, the supply of oil and all oil-derived products is reduced in proportion to the reduction in gasoline demand. Thus, these cases examine the potential for substitution of ethanol for gasoline and an equivalent reduction in refinery demand for oil.

Table 4-8 presents the results of these fixed-blend cases in terms of the sources of fuel ethanol. As expected from the data in Table 4-7, corn residues supply the initial ethanol demands; for ethanol contribution up to 2.5% (2 x 10^9 gal), all ethanol comes from the acid hydrolysis of corn residues. At the 5% level, all logging residues are used and corn grain supplies the remaining demand. At the 10% level, wood comes into the solution as the limit (in the base case) of corn used for ethanol is reached. To meet the 25% level of ethanol contribution to vehicle fuels, all wood is exhausted and 13% of the corn grain must be fermented to meet the 20 x 10^9 gal ethanol demand.* In all cases, the solution is feasible—all demands can be met even though oil and oil-derived products are reduced in proportion to the gasoline demand reduction. However, the structure of the industry changes somewhat to adjust to the changes in feedstock availablility. First, natural gas consumption increases to provide feedstocks for olefin production. Reduced oil availability reduces the supplies of oil-derived propane, butane, naphtha, etc., and natural gas refining must increase to make up the difference in feedstocks. Although the supplies of natural gas are more than sufficient to substitute for the reduced availabilities of petroleum products, forcing the model to utilize more expensive ethanol and natural gas makes it more expensive to fill final demands.

The relative objective function value over these cases provides a rough estimate of the cost of forcing (i.e., by legislative mandate, curtailment of imports) the economy to substitute ethanol for gasoline and reducing oil consumption accordingly. The relative cost of meeting fuels and chemicals demands varies only slightly from the base case to the 5% ethanol contribution. Naturally, the average cost per gallon of fuel is increased because the cost of ethanol is greater than that of gasoline. However, at low levels of ethanol

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*The base case constrains corn-derived ethanol to 10^9 gal. To reach this level of ethanol production, the constraint was relaxed, allowing all available corn grain (approximately 7 x 10^9 bu) to be used for ethanol. The level of corn-derived ethanol in solution requires approximately 13% of the available corn grain.

Table 4-8. Feedstock Contributions to Fixed-Blend Ethanol Demands[a]

Feedstock	Percentage of Fixed Blend Ethanol of 80 x 10^9 gal Fuel Demand					
	0.5%	1.25%	2.5%	5%	10%	25%
Corn residues	400	1,000	2,000	2,720	2,784[b]	2,784[b]
Logging residues						
Softwood	0	0	0	574[a]	574[b]	574[b]
Hardwood	0	0	0	469	483[a]	483[b]
Wood	0	0	0	0	3,160	13,779[b]
Corn grain	0	0	0	237	1,000[b]	2,381[c]
Total ethanol	400	1,000	2,000	4,000	8,000	20,000
Relative objective function value	1.00	1.001	1.002	1.008	1.03	1.13

[a] Entries are in 10^6 gal of ethanol contribution, by feedstock, to the fixed ethanol demands.

[b] Resource at base-case capacity.

[c] The base case constrains corn-derived ethanol to 10^9 gal. To reach this level of ethanol production, the constraint was relaxed, allowing all available corn grain (approximately 7 x 10^9 bu) to be used for ethanol. The level of corn-derived ethanol in the solution requires approximately 13% of the available corn grain.

contribution, the low-cost routes to ethanol predominate, and the marginal increment to average fuel cost is low. At higher levels of ethanol demand, more costly routes (wood and corn grain) are required, and the average fuel cost and total industry cost rise accordingly.

4.3.2.2 Free Market Ethanol Demands

The analyses in the previous section involved determining the effect of increasing the pool of ethanol exogenously. That is, the system was forced to substitute ethanol for gasoline, and the results therefore pertain to forced market penetration. In this section the free market is simulated; ethanol and gasoline compete for the (fixed) transportation fuel demand. The model seeks the minimum-cost solution for meeting final demands given the alternative processes, feedstocks, and costs.

The results of two different experimental designs are reported below. In the first design natural gas and oil prices are varied to examine the effect of increased nonrenewable feestocks on the role of ethanol in the optimized economy. The second design addresses the benefits derived from feedstock cost reductions and from process yield improvements.

Both of these experiments are run with two important constraints. The first relates to the role of fermentation ethanol. Currently, about 500 x 10^6 gal of ethanol production capacity is available for utilizing starch or sugar crops as feedstocks. As demonstrated above, the first acid hydrolysis capacity on line will probably compete with the existing corn grain capacity because of its cost advantages. However, to derive the potential for supplementing current corn grain ethanol with acid hydrolysis capacity, the model is restricted to utilizing all 500 x 10^6 gal of corn grain capacity in all experiments. This allows an examination of the capacity augmenting effects, but for this situation to materialize, corn fermentation plants would require a production subsidy (up to $1.00/gal) or cheaper corn (as low as $0.50/bu) to compete with corn residues in a proven commercial acid hydrolysis facility.

The second constraint involves the by-product credit for furfural. To derive a steady-state solution for the credit, the model was run with progessively lower furfural costs, starting at $0.29/lb, to determine the maximum furfural penetration. This occurred at $0.08/lb, where 2.48 x 10^8 lb are utilized. Given the fixed-proportion production rate of 3.5 lb furfural per gallon of ethanol, 710 x 10^6 gal of ethanol can be subsidized at a rate of $0.28/gal. According to the data in Table 4-7, the cheapest source of ethanol is corn residues. So, the model was supplied with 710 x 10^6 gal of corn residue-based ethanol at $0.91, but additional supplies were unsubsidized and therefore the cost reverts to the base case. As a result, all cases examined below show 958 gal of subsidized ethanol in the solution because it is priced below gasoline.

To summarize, the base case for the experiments reported below involves 500 x 10^6 gal of corn grain-based ethanol and 958 x 10^6 gal of subsidized (by furfural) corn residue-based ethanol. An additional penetration of ethanol can be ascribed to the particular parameters applied in a specific case.

Changes in Nonrenewable Feedstock Prices. Two experiments, the results of which are presented in Tables 4-9 and 4-10, examine the effects of nonrenewable feedstock prices. The data in Table 4-9 represent a doubling of the price of natural gas (Case A2), of oil (Case A3), and of both (Case A4). The most important result is evident in comparing Cases A2 and A3. With doubled natural gas prices only (A2), the only ethanol penetration is in the chemical demand market. Gasoline stocks are fully utilized and imports provide the remainder of the fuel demand. The 2.31 x 10^9 gal of ethanol brought into the solution are utilized for chemical-grade ethanol and for ethylene production. Thus, doubled real natural gas prices trigger demand for chemical ethanol and leave fuel markets unaffected with respect to petroleum feedstocks.

Conversely, with doubled oil prices only (Case A3), ethanol's highest value is as a fuel, and feedstocks are allocated to ethanol to displace gasoline until the higher-cost feedstocks no longer compete with $2.00/gal gasoline. Since the cheaper feedstocks are allocated to fuel, no ethanol is used in the production of chemicals. This switching that occurs when relative nonrenewable feedstock prices change emphasizes the interdependencies in the fuel and petrochemical industry.

Table 4-10 presents the results of increasing gasoline prices up to 100% while all other data are held at base-case levels. This represents the situation where demand pressure increases gasoline prices but not the value of other components of the barrel of oil. As the price of gasoline increases (in $0.25/gal increments), even more residues are utilized until, at $1.75/gal, the lower marginal cost of logging residues causes them to be utilized

Table 4-9. Optimal Fuel and Chemical Allocations for Various Oil and Natural Gas Prices

	Case			
	A1 (base)	A2	A3	A4
Natural gas price ($\$/10^3$ ft^3)	3.00	6.00	3.00	6.00
Oil price ($/bbl)	32.00	32.00	64.00	64.00
	Optimal Fuel and Chemical Allocation			
Gasoline				
Refined (10^9 gal)	79.289	79.615	64.772	64.772
Imports (10^9 gal)	0.0	0.385	0.0	0.0
	79.289	80.000	64.772	64.772
Ethanol				
Fuel (10^9 gal)	0.710	0.0	15.228	15.228
Chemicals				
Ethanol (10^9 gal)	0.0	0.200	0.0	0.0
Ethylene (10^9 gal)	0.0	2.110	0.0	0.0
	0.710	2.310	15.228	15.228
Furfural				
Furfural (10^6 lb)	140.00	140.00	140.00	140.00
Maleic anhydride (10^6 lb)	454.00	454.00	454.00	454.00
Adipic acid (10^6 lb)	1002.00	1002.00	1002.00	1002.00
Butanol (10^6 lb)	1758.00	1758.00	1758.00	1758.00
	3354.00	3354.00	3354.00	3354.00

(since only more expensive corn residue supplies are left). Finally, at $2.00/gal for gasoline (Case B5), all corn and logging residues are exhausted. And, since corn-based ethanol is cheaper than gasoline ($1.84/gal versus $2.00/gal), corn grain is brought into the solution at its capacity, over 7 x 10^9 bu to produce an additional 17.5 x 10^9 gal of ethanol. At this point, all cost-effective alternatives are exhausted (wood-based ethanol is priced at $2.05/gal), so gasoline fills the remaining demand.

These results point out the potential for severe food versus fuel conflicts if gasoline prices rise sharply, no demand reductions occur, and alternative fuel supplies are limited to those identified in the base case. To release this competition, extensive lignocellulosic feedstocks, such as short-rotation woody crops, must be developed to complement the acid hydrolysis technology.

Table 4-10. Optimal Transportation Fuel Mix at Various Gasoline Prices[a]

	Case				
	B1 (base)	B2	B3	B4	B5
Gasoline price ($/gal)	1.00	1.25	1.50	1.75	2.00
	Fuel Contribution in 10^9 gal				
Gasoline	78.541	77.190	76.939	75.964	58.477
Ethanol					
Corn residues (sub.)[b]	0.958	0.958	0.958	0.958	0.958
Corn grain[d]	0.500[c]	0.500[c]	0.500[c]	0.500[c]	17.705
Corn residues (unsub.)[e]	0.0	1.351	1.602	1.77	1.824
Logging residues[e]	0.0	0.0	0.0	0.807	1.037
Wood[e]	0.0	0.0	0.0	0.0	0.0
Total[f]	80.000	80.000	80.000	80.000	80.000

[a] Gasoline demand at 80 x 10^9 gal (excluding methanol and blenders).
[b] Ethanol via acid hydrolysis subsidized by furfural credit of $0.28/gal.
[c] Forced into solution to represent current capacity.
[d] Ethanol from corn grain available at base-case price and availability.
[e] Base-case feedstock cost and capacity and base-case production cost (unsubsidized).
[f] Independent rounding may result in discrepancies between entries and sums.

The Value of R&D Improvements in Acid Hydrolysis Technology. To examine the relative value of R&D alternatives for expanding ethanol fuel consumption, two additional experiments were conducted. First, ethanol yields were progressively increased from the base case to a 30% improvement. This replicates the effect of utilizing the xylose stream for ethanol rather than furfural and helps determine the benefits of R&D directed toward developing yeasts that ferment C_5 sugars. The results are presented in Table 4-11.

As an alternative, R&D could be directed at reducing the cost of feedstocks to make ethanol more competitive with gasoline. To examine this effect, corn residue costs were reduced progressively to 80% (case D2), 60% (case D3), and 50% (case D4) of the base-case costs, which varied regionally from $20-40/t (Table 4-12).

Decreasing the cost of residues to 60% or less of the base case, if other parameters are held constant, causes supplemental acid-hydrolysis ethanol to come into solution (Table 4-12). That is, in the base case only subsidized corn residues are cost-effective in producing fuel ethanol. But, at a cost of 60% of the base-case (D3), 1.6 x 10^9 gal of ethanol from corn residues displaces gasoline. At half the base-case cost (D4), this amount is increased to 1.85 x 10^9 gal. If this ethanol were to displace a proportionate amount of oil, 97 x 10^6 barrels of oil would be displaced annually for a savings, based on $32/bbl, of over $3 billion per year (not accounting for refinery costs).*

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*Assuming 42 gal (or one barrel) of oil and that 44% of the barrel is gasoline, then 42 x 0.44 = 19 gal of ethanol displacing one barrel of oil, assuming demands for other oil-based products are filled elsewhere.

Table 4-11. Optimal Transportation Fuel Mix at Various Yields of Ethanol from Corn Residue[a]

	Case			
	C1 (base)	C2	C3	C4
Ethanol yield (corn residue) (gal/t)	26.0	28.6	31.2	33.8
	Fuel Contribution in 10^9 gal			
Gasoline	78.541	78.541	76.728	76.497
Ethanol				
Corn residue (sub.)[b]	0.958	0.958	0.958	0.958
Corn grain[c]	0.500	0.500	0.500	0.500
Corn residue (unsub.)	0.0	0.0	1.813	2.044
Logging res.[d]	0.0	0.0	0.0	0.0
Wood[d]	0.0	0.0	0.0	0.0
Total[e]	80.000	80.000	80.000	80.000

[a] Gasoline demand at 80 x 10^9 gal (excluding methanol and blenders).

[b] Ethanol via acid hydrolysis subsidized by furfural credit of $0.28/gal.

[c] Forced into solution to represent current capacity.

[d] Base-case feedstock cost, availability, and production cost.

[e] Independent rounding may result in discrepancies between entries and sums.

By comparison, an R&D program that developed successful C_5 sugar fermentation could result in about 2.3 x 10^9 additional gallons of gasoline displaced, or benefits of over $3.8 billion in savings again, with the promise that other product demands can be met at the base-case costs. These crude estimates of the benefits of R&D point out the value of improving acid hydrolysis technology. However, given the large subsidy for furfural at a price of $0.10/lb ($0.35/gal ethanol), it appears that if additional markets for furfural can be devised, the returns of this effort will be even greater, given the limited opportunity for improving ethanol yield from xylose and the limits to improving corn residue collection costs.

4.4 SUMMARY

To summarize the impacts of a furfural credit on the selling price of ethanol and compare this research gain with the benefit derived from xylose fermentation, a base-case ethanol supply curve has been estimated. The effects of these R&D options are evaluated in terms of the ability of these options to improve the competitive position of ethanol from the base case. The base-case supply curve is constructed from the information in Table 4-8 and is drawn in Figure 4-2. The points along the supply curve show the quantities of ethanol that could be produced from lignocellulosic feedstocks and the corresponding ethanol selling prices. The curve is drawn as a step function because the prices of the feedstocks vary regionally and there are yield differences in the various feedstocks. The horizontal line segments measure the amounts of ethanol available at each price while the vertical line segments show the incremental price change required to make additional amounts of ethanol available. These price changes result from the depletion of the least expensive feedstocks.

Table 4-12. Optimal Transportation Fuel Mix at Various Corn Residue Prices[a]

	Case			
	D1 (base)	D2	D3	D4
Corn residue price (% of base)	100	80	60	50
	Fuel Contribution in 10^9 gal			
Gasoline	78.541	78.541	76.728	76.497
Ethanol				
Corn residue (sub.)[b]	0.958	0.958	0.958	0.958
Corn grain[c]	0.500	0.500	0.500	0.500
Corn residue (unsub.)	0.0	0.0	1.351	1.602
Logging residue	0.0	0.0	0.0	0.0
Wood	0.0	0.0	0.0	0.0
Total[d]	80.000	80.000	80.000	80.000

[a] Gasoline demand at 80 x 10^9 gal (excluding methanol and blenders).

[b] Ethanol via acid hydrolysis subsidized by furfural credit of $0.28/gal.

[c] Forced into solution to represent current capacity.

[d] Independent rounding may result in discrepancies between entries and sums.

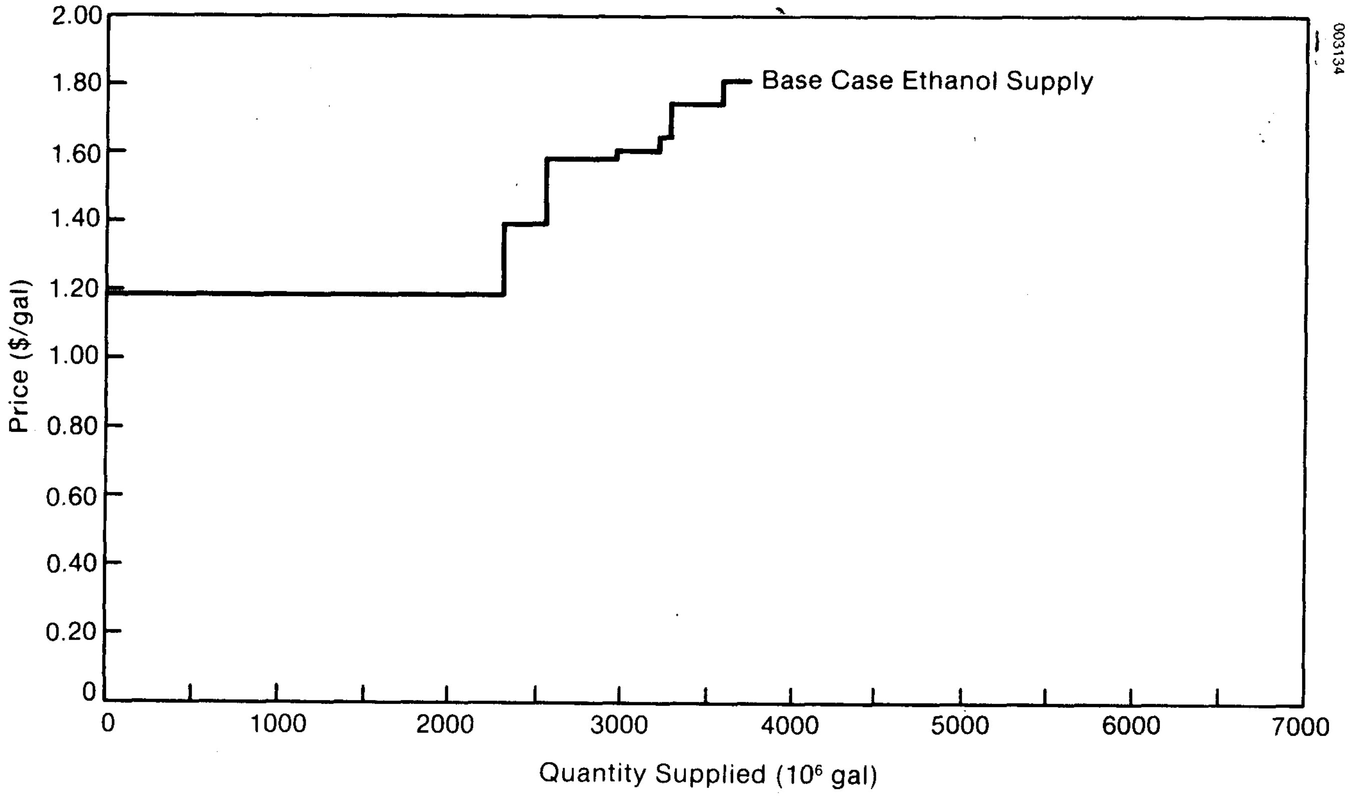
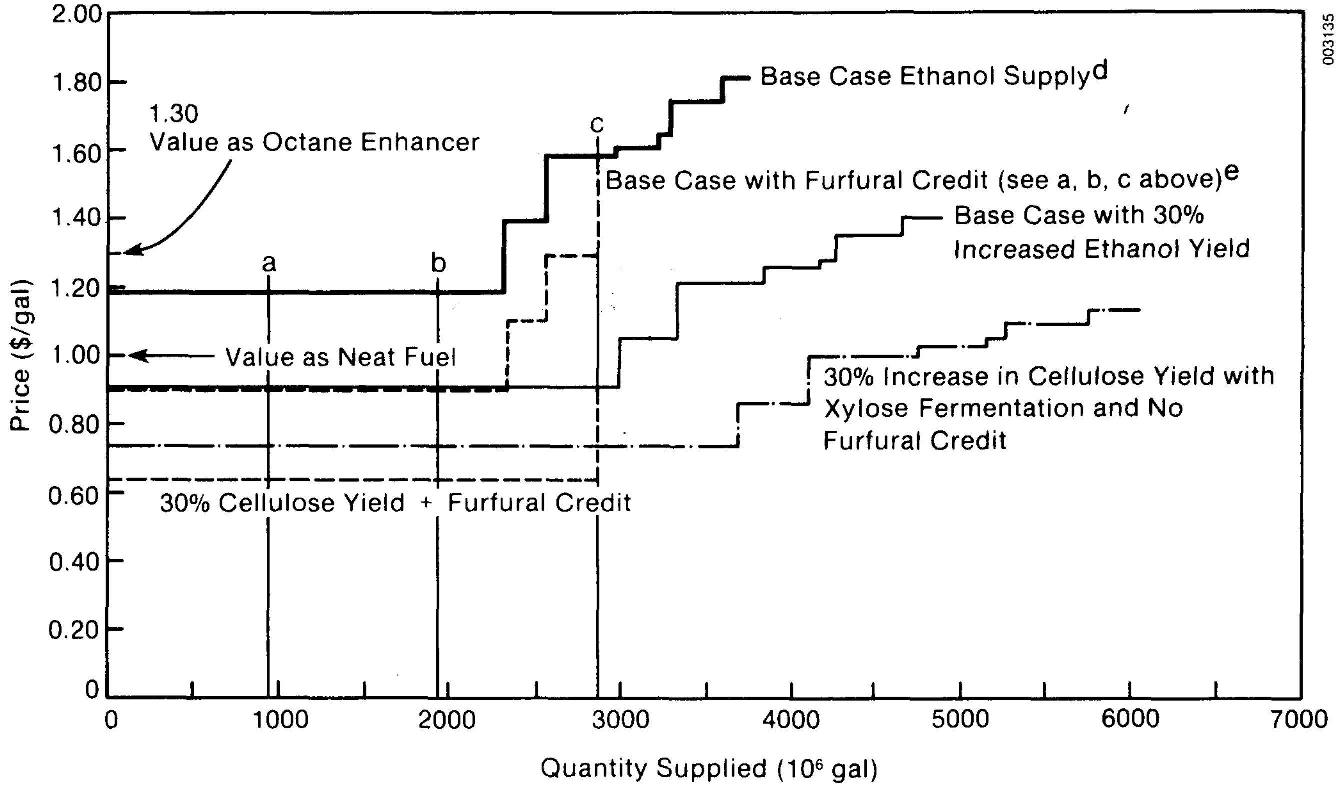


Figure 4-2. Base-Case Ethanol Supply Curve

Figure 4-3 depicts the base-case supply curve and the curves resulting from the furfural credit and xylose fermentation. In addition to the base case, three curves are drawn: the base case with a furfural credit, the base case with a 30% yield increase, and the base case with a 60% yield increase. Each case is discussed in greater detail in Sections 4.4.1, 4.4.2, and 4.4.3.

4.4.1 The Furfural Credit

With the assumptions of 3.5 lb of furfural produced per gallon of ethanol and selling for \$0.08/lb, the ethanol production cost credit is \$0.28/gal. Since the size of the furfural market being considered is 3354 x 10^6 lb, the price of approximately 960 x 10^6 gal of ethanol is reduced from \$1.19/gal to \$0.91/gal. Reference line a in Figure 4-3 is drawn to mark this 960 x 10^6 gal level. The furfural credit creates another step in the supply



a) This level of ethanol production corresponds to a furfural market of 3354 × 10^6 lb. This corresponds to the furfural demanded for adipic acid, maleic anhydride and furfural (see Table 4-1).

b) Based on a 100% increase in furfural market size

c) Based on a 200% increase in furfural market size

d) State-of-the-art ethanol production techonology with no furfural credit and given resource supply costs

e) Furfural credit of \$0.08/lb (\$0.28/gal)

Figure 4-3. Effects of Furfural Credit and Xylose Fermentation on the Base-Case Ethanol Supply Curve

curve. The first 960 x 10^6 gal are available at a lower price, and there are no other changes. Therefore, at ethanol levels greater than 960 x 10^6 gal, the base-case supply curve remains unchanged.

If additional markets for furfural could be developed, larger levels of ethanol production would earn a credit. Reference lines b and c show the effects of 100% and 200% increases in the size of the furfural market in terms of the larger levels of ethanol production that would earn a credit. The impact of this shift is that close to 1.0 x 10^9 gal of ethanol (which is competitive as an octane enhancer at a price of $1.19/gal) are competitive as a neat fuel at a price of $0.91/gal as a result of the credit. However, at $0.91/gal, ethanol is more than marginally competitive as a neat fuel. This competitive position might be maintained at prices as high as $1.00/gal. This implies substantial profit for the initial entrants into the production of ethanol and furfural. Corresponding to a 100% increase in the size of the furfural market is a level of ethanol production that is less than the total ethanol available at $1.19/gal. The effects of the furfural credit are therefore the same: ethanol that was competitive as an octane enhancer is now competitive as a neat fuel. At a 200% increase in the size of the furfural market, the balance of the lowest-cost ethanol is made competitive as a neat fuel and the next two more costly sources of ethanol, which were formerly not competitive as octane enhancers, become competitive as a result of the credit.

4.4.2 Thirty Percent Increase in Ethanol Yield

A 30% yield increase could be the result of research efforts—in xylose fermentation or increased cellulose yield from the feedstocks. Since xylose fermentation is a different use of the xylose stream, no furfural credit can be applied in addition to the gains from the xylose fermentation. As opposed to the furfural credit, which only lowers the price of ethanol, the 30% yield increase decreases prices and produces more ethanol. This causes the supply curve to shift down and to the right; indicating that just over 3 x 10^9 gal are competitive as a neat fuel and an additional 10^9 gal are competitive as octane enhancer as a result of the yield increase from xylose fermentation. The 30% yield increase could also be the result of a longer cellulose recovery. The shift of the supply curve is the same as that for xylose fermentation except that it is also possible to incorporate the different uses of the xylose fraction. The downward shift of this curve results from the effect of the $0.28/gal furfural credit on the levels of ethanol production, as denoted by reference lines a, b, and c. Past point c, no credit is earned and the remainder of the supply curve is unchanged. As a result of the increased ethanol yield, the least-cost ethanol is now increased from about 2.3 x 10^9 gal to 3.0 x 10^9 gal. This allows the furfural credit earned from a 200% increase in the furfural market to be earned completely by the ethanol produced by the least-cost feedstock. In this case, the ethanol cost is lower than that from any other case, with 3 x 10^9 gal priced below $0.70/gal. Again, since this ethanol could be priced close to $1.00/gal, the furfural credit is a large source of profit for the producers of the first 3 x 10^9 gal of ethanol.

4.4.3 Sixty Percent Increase in Ethanol Yields

This final case is a result of assuming the first 30% yield increase to be a result of increased cellulose recovery and augmenting it with an additional 30% increase in yield resulting from fermentation of the xylose fraction. In this case no furfural credit is possible. Compared with the case where a furfural credit is earned, the price reduction is lower but greater quantities are available. The xylose fermentation reduces ethanol costs to below $0.80/gal and increases the availability of ethanol at this price to over 3.5

x 10^9 gal. Because the furfural credit does not have an influence on the entire supply curve, the greatest ethanol market penetration will result from the combination of increased cellulose recovery and xylose fermentataion. Over 5 x 10^9 gal of ethanol are competitive as a neat fuel as a result of this combination of research gains.

In conclusion, it appears that furfural's best contribution will be as a source of intermediate-term profit for ethanol/furfural producers. This profit will serve as a strong incentive in the development and implementation of the acid hydrolysis technology. The maximum ethanol penetration in the longer term, however, will result from technologies capable of increasing ethanol yields.

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SECTION 5.0

CONCLUSIONS AND RECOMMENDATIONS

Furfural is an economically attractive coproduct in the acid hydrolysis of cellulose for fuel-grade ethanol production, provided large-volume markets can be developed. A single 50 x 10^6 gal/yr ethanol plant would produce 140 to 200 x 10^6 lb/yr of furfural, an amount equal to the total current domestic market. Thus, new outlets for furfural in substantial quantities would be needed to support large-scale development of an ethanol-from-cellulose industry. Furfural is a versatile, reactive chemical with a history of utility as a precursor that predates the petrochemicals era. This study uncovered some of the old laboratory work on upgrading furfural and established its present-day economic potential as a large-volume, low-cost by-product.

This study indicates a favorable economic prognosis for manufacture of n-butanol, adipic acid, and maleic anhydride from furfural. The information used to make the appraisals is old and of uncertain quality, and in no case did it go beyond laboratory demonstrations of the chemical reactions. Nevertheless, the results indicate that these primitive processes have enough profitability potential to ultimately displace the conventional hydrocarbon-based processes and provide significant support to the economics of fuel-grade ethanol. Justification appears to be quite adequate for a continuing research program to improve the definition of the three processes of interest.

The analysis of furfural potential, within the context of an optimally organized fuels and chemicals industry, indicates that the three most attractive processes could subsidize approximately 960 x 10^6 gal of ethanol to a selling price as low as \$0.91/gal. This ethanol cost is based on a furfural credit of \$0.28/lb and utilization of the lowest-cost biomass feedstocks (corn residues at \$20/ton). However, this production level exhausts slightly less than one-half of the available corn residues, the most economic feedstock for ethanol production. If additional furfural markets of about 5 x 10^9 lb, with a value of at least \$0.08/lb, could be identified, then over 2.5 x 10^9 gal of ethanol could be marketed at about \$1.00/gal. With respect to this prospect, the phenolic resin market is another possible outlet for large quantities of furfural. Current domestic volume is 1.2-1.5 x 10^9 lb/yr with prices in the \$2.00-\$2.50/lb range. The market has been dominated since its beginning by phenol-formaldehyde formulations and has become firmly established on this foundation. Also long known is that furfural, an aldehyde, can be substituted for formaldehyde to yield a different group of thermo-setting phenolic resins. A related potential new product group could be furan resins, based on substitution of furfural alcohol (from furfural) for phenol. A large number of formulations were invented many years ago, but they remain undeveloped. It is possible that, given very low cost furfural, a new competitive line of phenolic resins would find a place in the market. However, estimates of such penetration are difficult to estimate because of the complex interactions of formulations, performance properties and prices, and the traditional and strong resistance of the resin business to changes of any kind. Investigation of furfural's place in the thermo-setting resin business was beyond the scope of this study, but could be done as a separate, future project. Process technology and marketing studies would necessarily be considerably more extensive than in the relatively straightforward appraisal of commodity chemicals in this study.

Converting the xylose stream to ethanol has about the same effect on the selling price of ethanol as the furfural credit. The major difference between these two research options is the increased availability of ethanol at each price through xylose fermentation, while the furfural credit only lowers the price of given levels of ethanol. However, the impact of xylose fermentation is restricted to the fuels markets, while the furfural credit not only makes ethanol more competitive, but also substitutes for other petroleum-based products that are chemical precursors. The greatest ethanol penetration will result from the xylose fermentation, while the furfural credit offers large near-term profits as an incentive to ethanol producers and has a more diversified impact on reduced petroleum product demand.

A recommended program to expand furfural markets would initially include the following general elements:

- Comprehensive literature search for work on furfural-upgrading chemistry, covering at least the past 75 years. The prime reference will be, as it was in this study, the American Chemical Society monograph, The Furans, by A. P. Dunlop and F. N. Peters of the Quaker Oats Company. A special effort would be made to examine German, Russian, and more recent Japanese sources. Feasibility studies similar to those made for this report would be made on additional processes identified as potential candidates.
- Experimental bench-scale verification of literature-source process data on a selective basis, to be done concurrently with the literature search and extending beyond it if appropriate.
- Industrial liaison investigation into pertinent past and current work in the organic chemicals industry, both domestic and foreign. This effort might include a budget for selective purchase of consultants' studies, and possible travel expense to obtain unpublished information through informal industry contacts.
- Exploratory pilot-scale development work on a field-test-laboratory scale to improve definitions of process operability, safety, and profitability and to enhance understanding of all process parameters. All viable furfural derivatives would be studied.
- Process engineering studies of results of laboratory work in the context of projected large-scale manufacturing facilities to determine the effects of operability, safety, and profitability considerations on process definitions.
- Transfer of technology to a private enterprise, if a viable project can be defined, for continuation of engineering and construction to commercialization.

The projected economic synergism of fuel-grade ethanol and upgraded furfural manufacture indicates the need for integration of future research and process engineering into a single, coordinated program. In addition, future work on furfural development should be broadened to include lignin. Lignin is another potentially high-value by-product of the cellulose hydrolysis ethanol process. High quality and a volume of several billion pounds per year would characterize the lignin from a future lignocellulosic fuel ethanol industry. Its most important derivatives would most probably be commercial-grade phenol and benzene. Production of these chemicals from lignin could have sufficiently high volume and low cost to have significant impact on their billion-pound markets. Future ethanol process studies of technology, economics, and market potentials should include the contribution of lignin and its derivatives.

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APPENDIX A

PROCESS ENGINEERING STUDIES

APPENDIX A

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A.1 INTRODUCTION

This appendix presents the detailed engineering studies of conventional (i.e., hydrocarbon-based) and furfural-based processes for the large-scale production of each of the five chemicals under consideration. These studies were prepared by Energy Technology Associates (ETA) under subcontract to SERI.

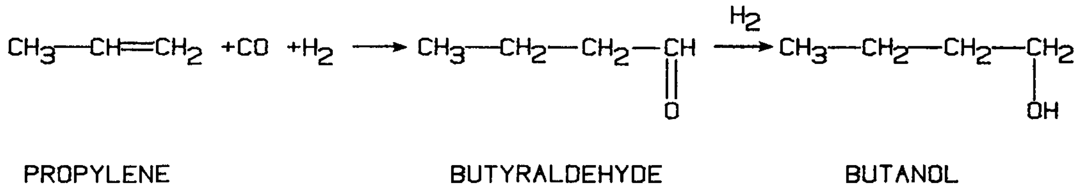
The hydrocarbon-based processes are presented first. The furfural-based processes are presented next, starting with the conversion of furfural to furan and THF. These are followed by a discussion of the bases for estimation of capital investment and production costs as well as the selling price required for a nominal 15% annual return on investment. Finally, the cost of production summary sheet is presented for each process; where the feedstock cost is varied, more than one summary sheet is presented for some of the processes.

A.2 PETROCHEMICAL ROUTES

A.2.1 Hydrocarbon-Based Technology for n-Butanol

A.2.1.1 Process Chemistry

Butanol production processes currently use catalyzed carbonylation of propylene (the oxo process). Two catalyst systems are in current use: cobalt and rhodium. The more modern rhodium-based catalysts appear to have an advantage for new plants because they allow lower operating pressures and give higher yields of n-butanol. The first step is to form butyraldehyde by carbonylation. Hydrogenation of this intermediate, simultaneously or separately, gives n-butanol:



$$CH_3\text{—}CH\text{=}CH_2 + CO + H_2 \longrightarrow CH_3\text{—}CH_2\text{—}CH_2\text{—}\underset{\underset{O}{\|}}{CH} \xrightarrow{H_2} CH_3\text{—}CH_2\text{—}CH_2\text{—}\underset{\underset{OH}{|}}{CH_2}$$

The catalyst system is homogeneous. The active form is either rhodium carbonyl or phosphine(or amine)-modified rhodium carbonyl. Modified rhodium catalysts allow lower pressures than unmodified catalysts, but they require higher temperatures because of the considerably slower reaction rates. There is some hydrogenation of the olefin feedstock to propane with either catalyst. Hydrogenation of the aldehyde to alcohol in the carbonylation reactor is essentially quantitative but can be varied from nearly 0% to almost 100% (Shell 1968). When the hydrogenation reaction is performed separately, suitable catalysts are Raney nickel, Raney copper, copper chromite, cobalt phosphine complexes, or nickel-on-kieselguhr. The process description for the rhodium phosphine-catalyzed process is presented here because it offers the best current economics for extrapolation to 1995.

A.2.1.2 Process Design

A process flow diagram for the production of butanol via rhodium-catalyzed carbonylation is presented in Figure A-1. A partial oxidation plant supplies synthesis gas having a hydrogen to carbon monoxide ratio of 1.02. Packed-bed columns filled with zinc oxide desulfurize the gas. The level of sulfur is maintained below 1 ppm to reduce poisoning of the rhodium catalyst.

A molecular-sieve dryer removes trace quantities of water and dienes from the liquid propylene feedstock (94.5 wt % propylene). Water is removed to allow use of inexpensive materials of construction in the reactor system. The liquid propylene can be either injected directly into the reactors or combined with recycle propylene/propane.

The active catalyst complex in the two reactors, $HRh(CO)_2(PO_3)_2$, is formed in the reactor itself by the reaction of the synthesis gas with a rhodium salt and triphenylphosphine. A 10:1 ratio of normal to isoaldehyde in the reactor product requires a very high ratio of ligand (triphenylphosphine) to active catalyst complex. The concentration of triphenylphosphine in the reactors is several weight percent. Triphenylphosphine ligand and rhodium make-up are blended into the catalyst storage tanks; they then pass to the reactors. Dissolution of the catalyst make-up and spent catalyst purge to maintain activity in the reactors are accomplished by taking a slipstream from the reactors. Two full charges of rhodium catalyst are required for the plant: one in the reactor and a spare, held in storage for make-up.

A common spare 304L stainless steel recycle-gas compressor is provided in the dual-train reaction system. A turbine agitator, top-mounted on each reactor, helps prevent coagulation of the catalyst and transfers the heat of reaction to the submerged cooling coils. The liquid level is held at one-half of the reactor volume to provide disengagement space for entrained liquid droplets.

The crude vapor product with the unreacted syngas and propylene passes overhead to the entrainment separators. Catalyst is recycled to the aldehyde reactors by gravity flow from the liquid trap.

The process is operated at low conversion of the feed gases, partly to provide a large enough volume of recycle gas for stripping of the reaction products, including the heavier by-products.

Reactor temperature and pressure are controlled by regulating the cooling water flow to the exchanger that cools the recycle gases. The concentration of recycled propane is maintained at a constant level by a controlled purge from the recycle stream. If polymer-grade propylene is the feedstock, a lower conversion per pass is necessary to ensure that enough gas is recycled to get adequate stripping, but there would be less propylene lost in the purge stream.

The crude, liquefied product is fed to the stripping column. Unreacted propylene plus propane is recycled to the reactor from the column overheads. The bottoms from the stripping column are cooled to 60°C and combined with hydrogen at 150 psi. This stream enters the aldehyde hydrogenation reactor, which is packed with 40 wt % nickel-on-

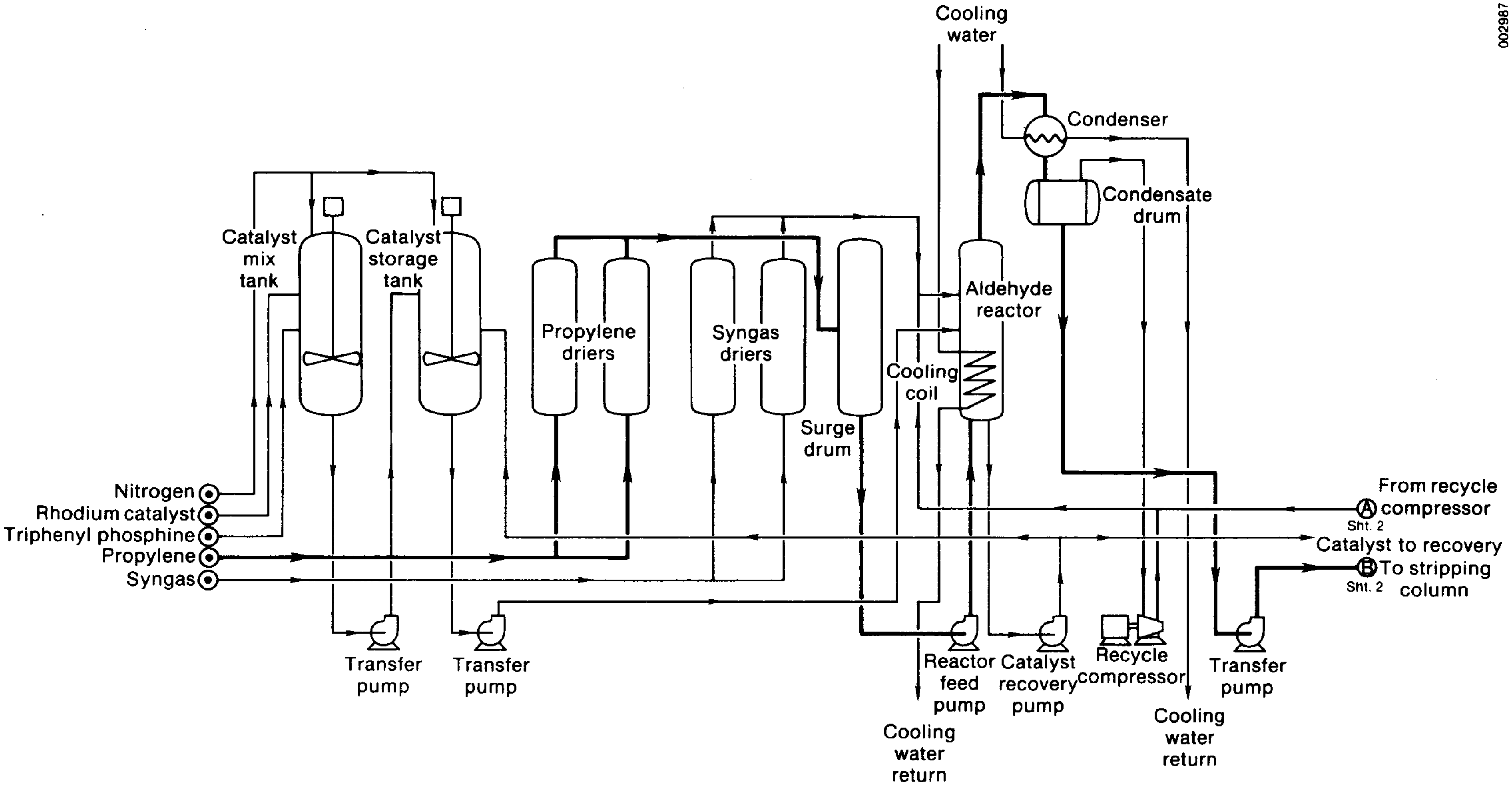


Figure A-1(a). **Process Flow Diagram for Production of n-Butanol from Propylene** (sheet 1 of 3)

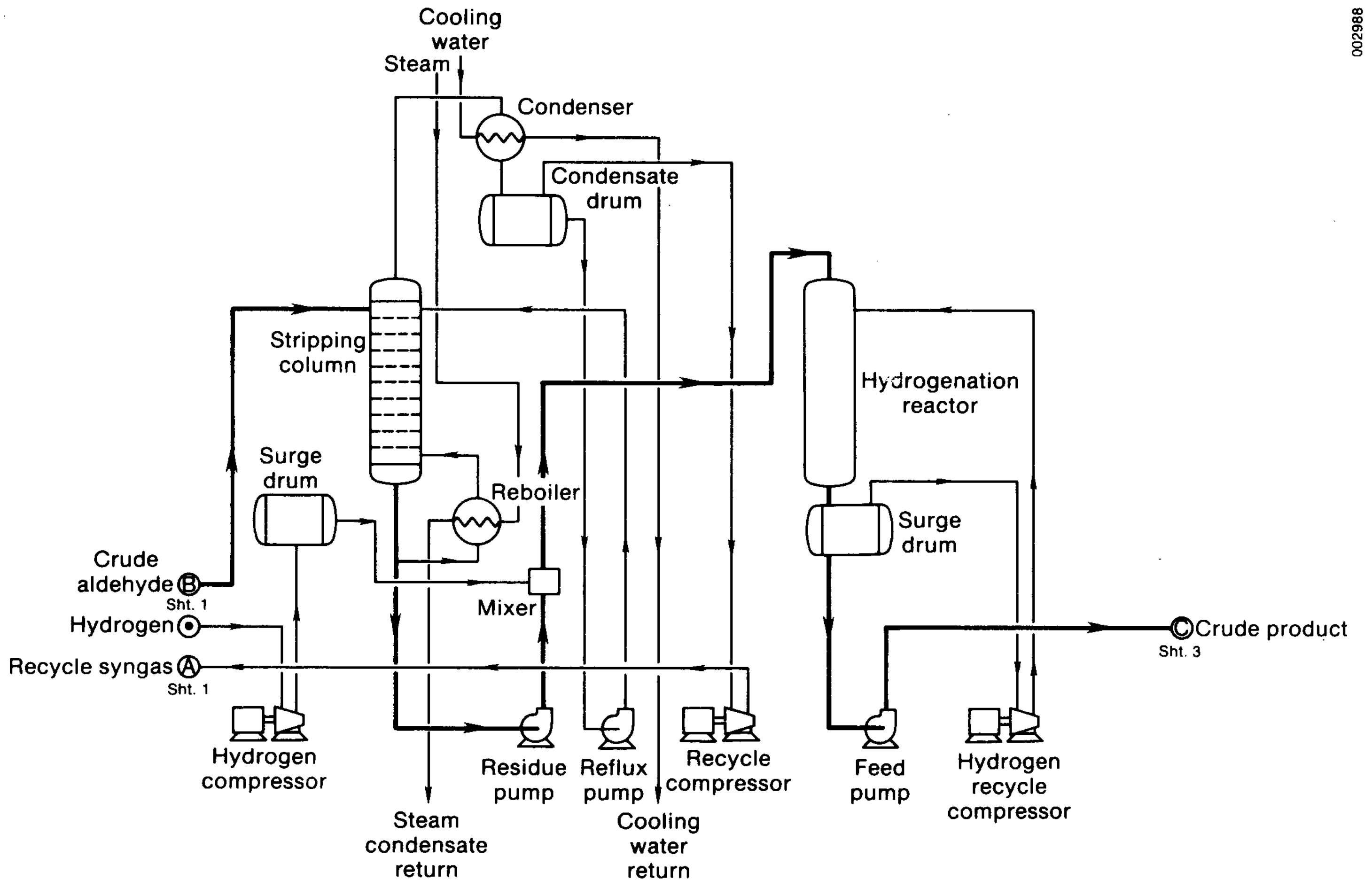


Figure A-1(b). **Process Flow Diagram for Production of n-Butanol from Propylene** (sheet 2 of 3)

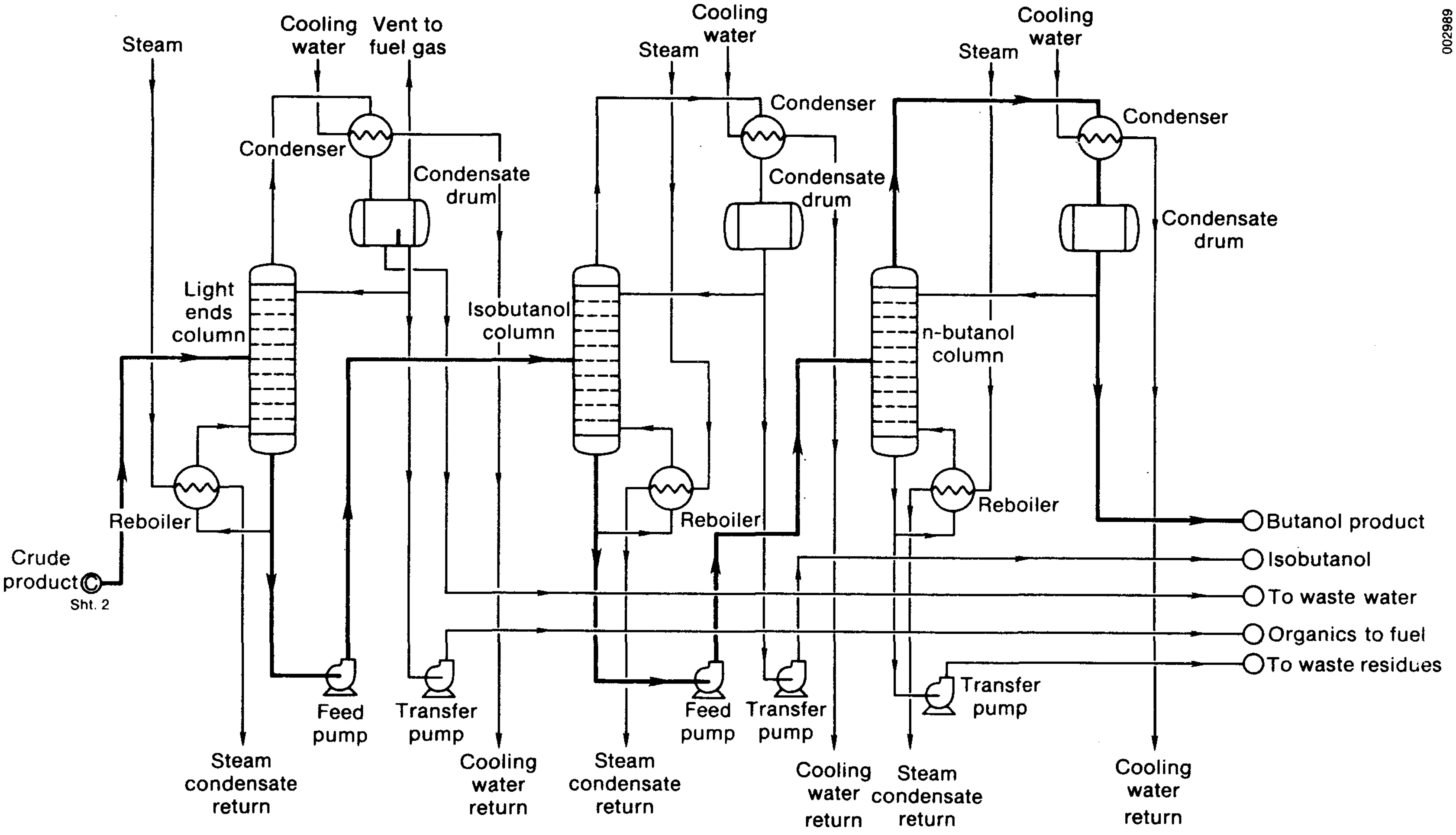


Figure A-1(c). **Process Flow Diagram for Production of n-Butanol from Propylene (sheet 3 of 3)**

kieselguhr. Approximately 4 moles of hydrogen are used per mole of feed. Unconverted hydrogen is recompressed and recycled.

Hydrogenation product (dissolved gases, butanols, and water) is then fed to the butanol distillation section. Dissolved gases, light ends, and water are taken overhead from the light ends column for disposal. The organic waste layer from the reflux drum goes to disposal.

Two columns are used to separate isobutanol and n-butanol. In the first, isobutanol is taken overhead with a purity of 99.8 wt %. In the second, the n-butanol is also an overhead product with a purity of 99.9 wt %. A heavies stream is withdrawn as residue and is purged to disposal.

A.2.2 Technology and Economics of 1,3-Butadiene from Hydrocarbons

1,3-butadiene was first obtained over 100 years ago by pyrolysis of petroleum hydrocarbons. Principal production processes for butadiene in the United States are steam cracking of naphtha and gas oil fractions, catalytic dehydrogenation of n-butene and n-butane, and oxidative dehydrogenation of n-butene. As additional steam cracking plants are built to meet a growing demand for ethylene and other lower olefins, they will become the dominant source of butadiene.

A.2.2.1 Chemistry of Steam Cracking

Thermal cracking of hydrocarbons in the presence of steam at 700°-900°C is a principal source of ethylene and other olefins and diolefins. Residence times are short, and steam-hydrocarbon weight ratios are generally in the range of 0.2 to 0.8. Conditions depend on the hydrocarbon composition of the feed stock and on the severity of operation desired. Ethylene can be produced from a wide range of hydrocarbon feed stocks including ethane, propane, butane, naphthas (i.e., fractions boiling up to about 230°C), gas oils (i.e., fractions boiling in the range of about 315°-480°C), etc. With naphthas and heavier feedstocks, the C_4 fraction of the product contains appreciable quantities of butadiene. Yield data for butadiene obtained by the steam cracking of various feedstocks at high severity, with recycle ethane cracking to extinction, are shown in Table A-1.

Table A-1. Butadiene Yields from Steam Cracking at High Severity

Feedstock	Once-Through Ethylene Yield (wt %)	Ratio[a]
Ethane	48.2	2.5
Propane	34.5	7.2
n-butane	35.8	8.7
Medium-range naphtha	30.0	13.6
Atmospheric gas oil	23.0	17.6
Light vacuum gas oil	18.0	26.2

[a] kg butadiene per 100 kg ethylene.
Source: Schleppinghoff 1974.

A.2.2.2 Process Design

The hydrocarbon conversion processes yield a crude C_4 fraction containing butadiene and other close-boiling hydrocarbons (Table A-2). For synthetic rubber manufacture a 99.0 wt % minimum purity butadiene is needed with acetylenes in the ppm range. Acetylenes are particularly undesirable because they can polymerize, contributing to equipment fouling and foaming problems.

Commercially, two methods are used for the separation and purification of 1,3-butadiene. One is selective extraction with aqueous cuprous ammonium acetate, the CAA process, which produces high-purity butadiene with a recovery higher than 98%. In the other method, butadiene is extractively distilled with selective solvents, including acetonitrile, furfural, dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, β-methoxypropionitrile and others. Furfural seems the appropriate choice here to relate the conventional to the novel synthesis routes.

Table A-2. Composition of a Crude Butadiene Fraction[a]

Component	Boiling Point (°C)	Vol %
C_3 hydrocarbons		0.9
Isobutylene	-6.9	27.7
1-butene	-6.3	17.2
1,3-butadiene	-4.4	39.1
n-butane	-0.5	4.1
trans-2-butene	+0.9	6.0
cis-2-butene	+3.7	4.5
C_4 acetylenes	+5.1	0.2
1,2-butadiene	+10.9	0.1
C_5 hydrocarbons		0.1

[a] Composition varies with process and conditions.
Source: Reis 1970.

A two-stage extractive distillation process is employed. Butadiene and acetylenes are first separated from the butenes and butanes, and then butadiene is separated from the acetylenic compounds.

A.2.3 Conventional Technology for Styrene

A.2.3.1 Ethylbenzene via Vapor-Phase Alkylation of Benzene

Chemistry of Benzene Alkylation. The currently most-favored vapor-phase alkylation process has been developed by Mobil and Badger, based on Mobil's ZSM-5 synthetic zeolite catalyst. Ethylene and benzene are reacted over the catalyst to form ethylbenzene, as in the older liquid-phase processes. The vapor-phase mode of operation has the major advantage of more efficient heat recovery at higher operating temperatures.

Catalyst recovery and product purification operations are also simpler, and the reaction environment is far less corrosive.

The alkylation catalyst capability of zeolites has been known for many years. Only in recent years has work to develop processes succeeded because the catalysts had been rapidly deactivated by coke formation and they were unable to transalkylate polyethylbenzenes. The Mobil-Badger process has reduced these problems to an acceptable level and has now been commercialized.

Bronsted acid sites on the zeolite catalysts activate the benzene molecules for the subsequent alkylation reaction. Then bonding with ethylene molecules occurs. In large pores, alkylation proceeds to polyethylbenzenes; forming these products reduces yield and also leads to coking.

In Mobil ZSM-5, the pore openings are elliptical, with a major axis of about 7 angstroms and a minor axis of about 5 angstroms (Chen and Garwood 1978). The pore opening has great shape selectivity, allowing molecules of ethylbenzene to diffuse freely, but restricting polyalkylated molecules. Additionally, the internal pore dimensions are small enough to create steric hindrance of toluene alkylation relative to benzene.

Reactor inlet temperature and feedstock composition are most significant in controlling conversion to ethylbenzene. Reaction by-products are di- and triethylbenzenes. The variable ratio of these products to ethylbenzene ranges from 1:7 to as little as 1:25, depending on the reaction pressure (Table A-3). These by-products are readily converted to ethylbenzene by transalkylation with benzene.

Table A-3. Ethylbenzene Selectivity as a Function of Reactor Pressure

	Pressure (psig)	
	0	50
Catalyst weight (g)	3.84	3.84
Ethylene rate (g mol/h)	0.207	0.207
Benzene feed rate (g mol/h)	9.16	9.10
Reactor inlet temperature (°C)	400	400
Maximum observed reactor temperature (°C)	438	435
Product weight (g/h)	155.2	156.8
Liquid product composition (wt %)		
Ethylbenzene	9.34	12.93
Diethylbenzenes	0.80	0.53

Source: Mobil 1979.

Process Description for Benzene Alkylation. A flowsheet for the Mobil-Badger process is shown in Fig. A-2, sheets 1 and 2.

The reactor operates at 425°-450°C and 260 psig, with a weight hourly space velocity (WHSV) of about 150 lb/h lb catalyst and a benzene/ethylene ratio ranging from 8 to 16. It is a four-bed system. Superheated benzene, ethylene, and recycled diethylbenzene are fed to the top bed. Additional ethylene and cooled benzene vapor are injected between

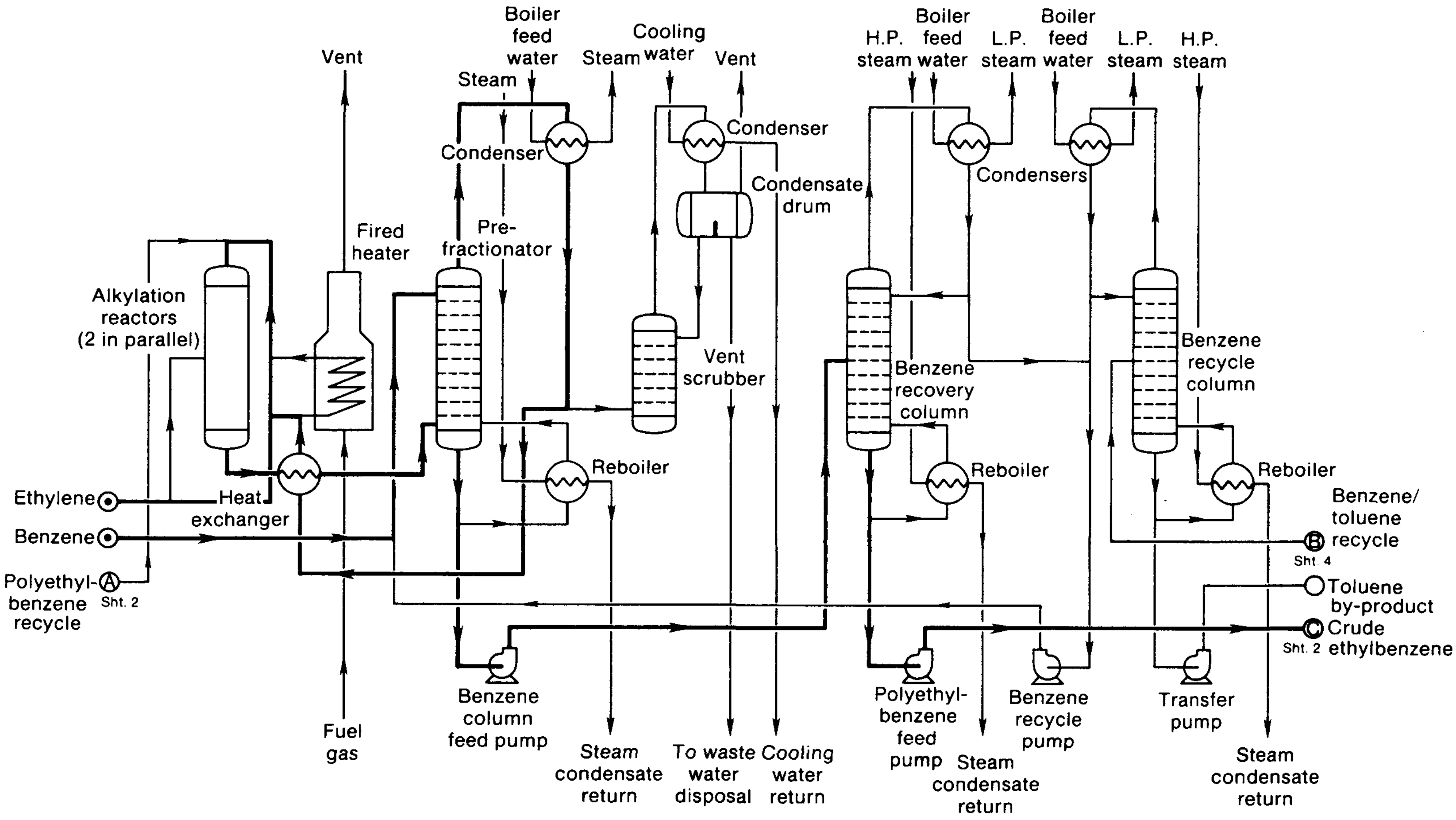


Figure A-2(a). **Process Flow Diagram for Production of Styrene from Benzene** (sheet 1 of 4)

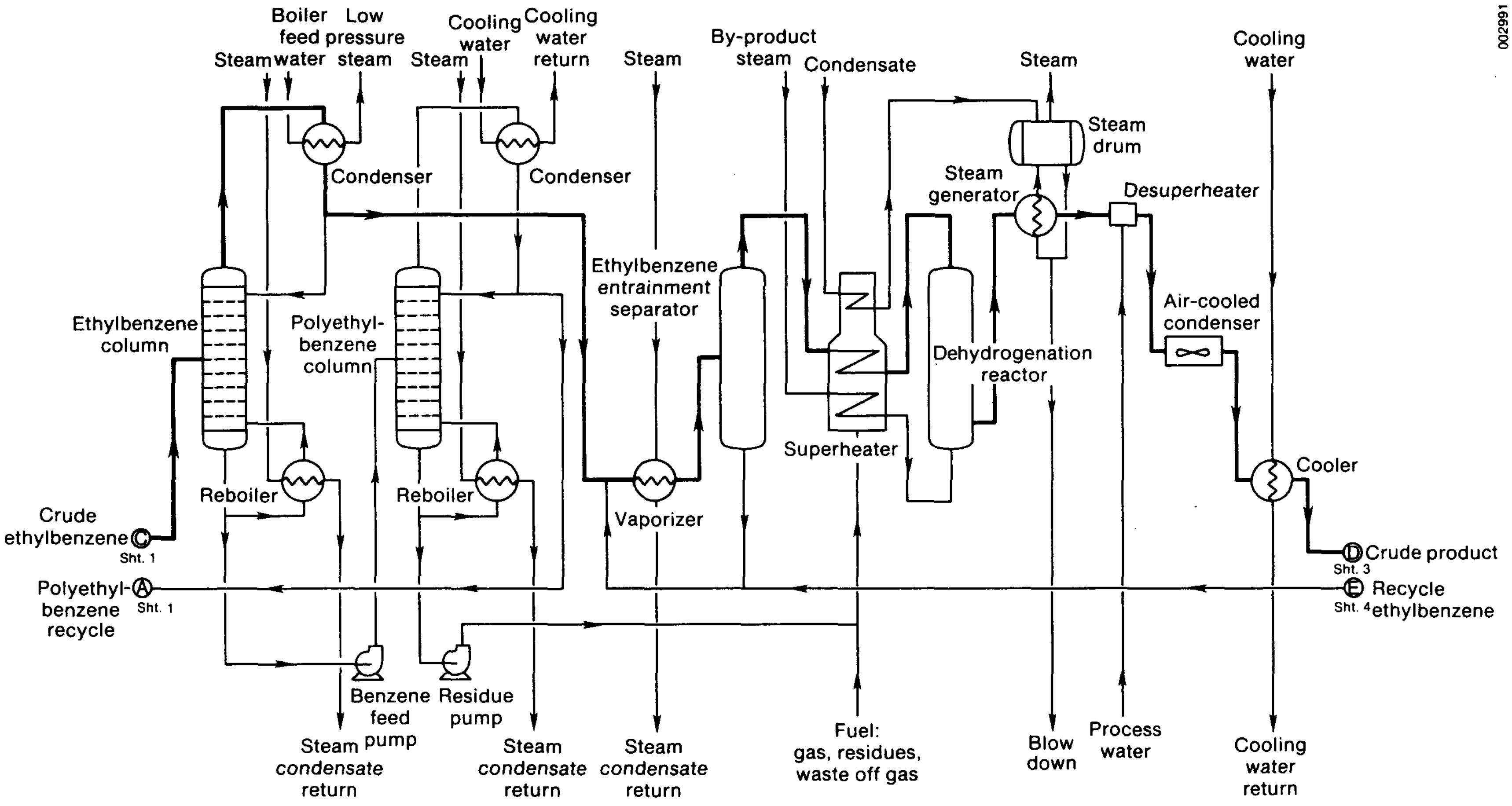


Figure A-2(b). **Process Flow Diagram for Production of Styrene from Benzene** (sheet 2 of 4)

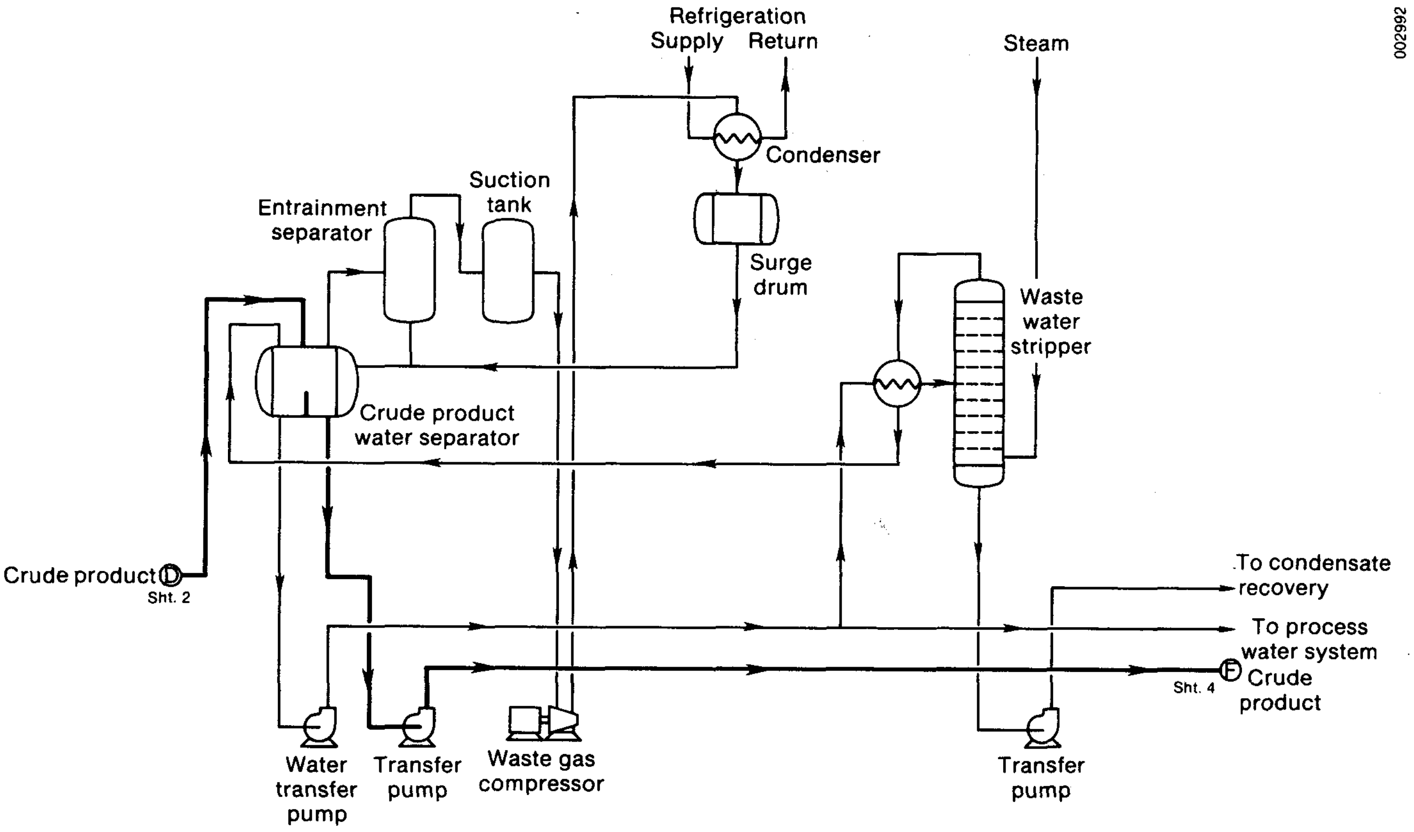


Figure A-2(c). **Process Flow Diagram for Production of Styrene from Benzene** (sheet 3 of 4)

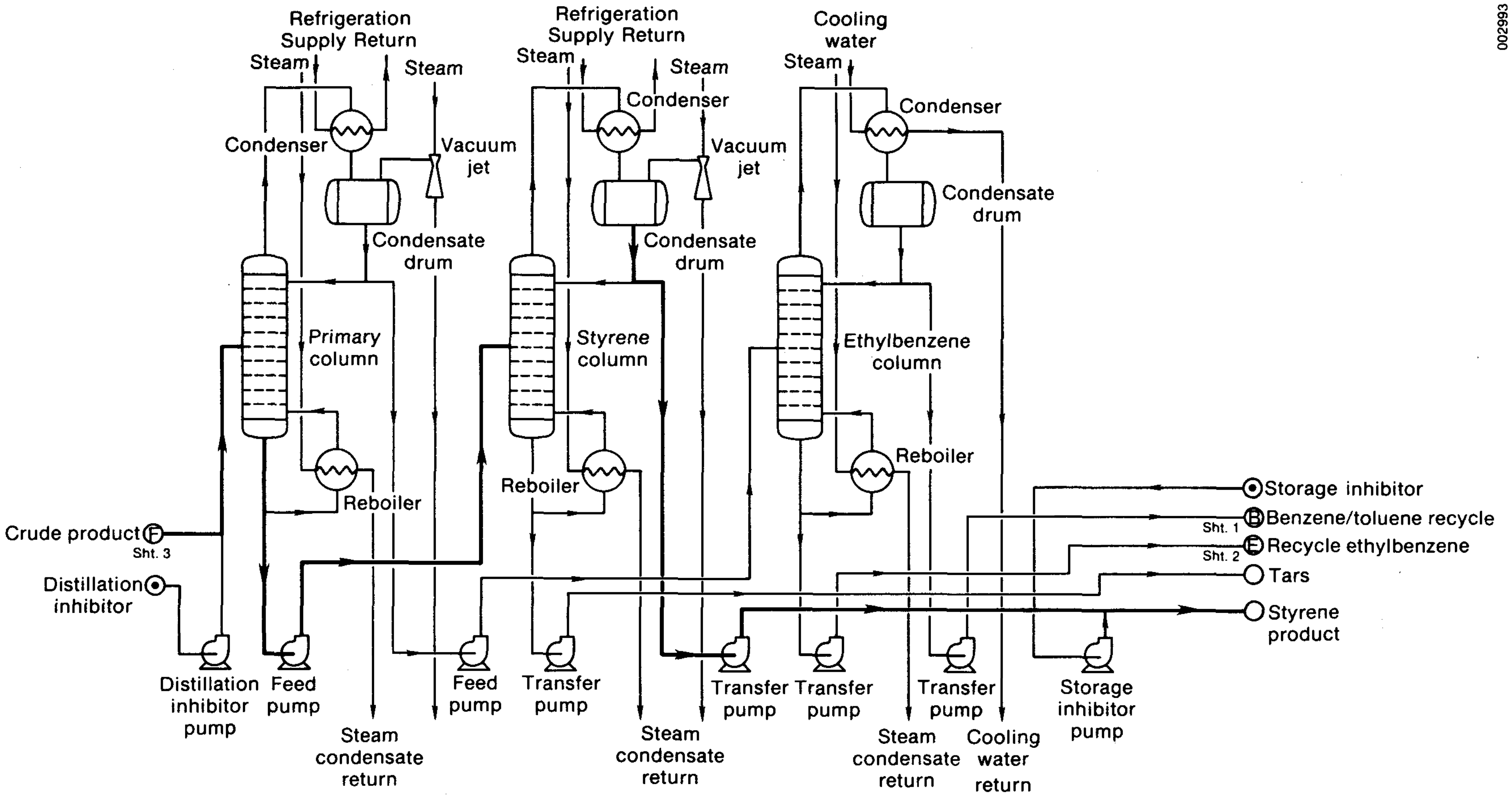


Figure A-2(d). **Process Flow Diagram for Production of Styrene from Benzene** (sheet 4 of 4) the beds to maintain a close approach to top-to-bottom isothermal conditions. About 99% selectivity to ethylbenzenes is obtained per pass. A swing reactor is installed to allow for coke burnoffs.

Reactor effluent heat is used to vaporize the recycle benzene in a heat exchanger before it passes to a prefractionator column, where the bulk of the benzene is separated. The column reflux is make-up benzene. Overheads are cooled, generating medium-pressure steam. Condensed benzene is recycled to the process through the vaporizer. Vapor from the condenser (medium-pressure steam boiler) is scrubbed, cooled, and recycled to the prefractionator.

The bottoms stream from the prefractionator passes into the separator, where the remaining benzene and toluene boil up overhead. A second column separates benzene from toluene, and the benzene is recycled. In a third column, the ethylbenzene is separated from polyethylbenzenes (mainly diethylbenzene), which are then recovered in a fourth column and recycled to the reactor for transalkylation with benzene.

Overall conversions in excess of 99% are claimed and 95% of the process heat input and reaction heat are recovered as low- or medium-pressure steam. Catalysts seem to be long-lived, even though carbon burnoff at two- to four-week intervals is necessary. Materials are carbon steel except for the reactor, where the burnoff temperatures require use of higher-grade steels.

A.2.3.2 Dehydrogenation of Ethylbenzene to Styrene

Chemistry of Ethylbenzene Dehydrogenation. Direct catalytic dehydrogenation of ethylbenzene is the commercial technology for styrene production. Ethylbenzene is catalytically dehydrogenated to styrene and hydrogen in the presence of steam. Toluene and benzene are formed as by-products. The steam is condensed and the organic components are separated by distillation. The overall reaction is endothermic with heat supplied by the steam (adiabatic reactors) or from external sources (isothermal reactors).

The apparent simplicity of the chemistry conceals practical difficulties. Yields are higher at low partial pressures, so the reaction is generally conducted under partial vacuum. Reaction temperatures are high, between 550° and 620°C, so rapid quenching of reaction products is necessary to minimize by-product formation. Because styrene is readily polymerized at higher temperatures, mixtures containing styrene must be distilled at reduced pressures in the presence of inhibitors to keep the reboiler temperature at an acceptable low level. The process consumes energy, so careful selection of conditions and extensive heat recovery is necessary to reduce the conversion costs.

The performance of the dehydrogenation catalyst determines the process economics. Desirable catalyst properties would give the following conditions:

- Low ratio of steam to ethylbenzene
- High selectivity to styrene
- Low by-product production, especially of toluene
- Low coking tendency
- One year between catalyst changes
- High mechanical stability and strength

- Low pressure drop.

Modern catalysts have the following five component:

- A major active ingredient, usually greater than 50%, chosen from oxides of iron, cobalt, manganese, chromium, or zirconium
- A stabilizer, which may be aluminum, magnesium, beryllium, calcium, barium, strontium, chromium, manganese, bismuth, cerium, molybdenum, tin, or rare earth oxides
- A carbon inhibitor, usually an oxide of potassium, rubidium, or another alkali metal
- A secondary promotor such as copper, silver, cadmium, thorium, or vanadium
- A cementing diluent such as calcium aluminate.

Currently several catalyst formulations are available from both Shell and United Catalysts to satisfy particular operating requirements. Others are known to be under development.

Inhibitors. Since styrene polymerizes readily, inhibitors must be used in both manufacture and storage. Two inhibitors, both effective only in the presence of oxygen, are 4-tertiary-butylcatechol (TBC) and hydroquinone. In the manufacturing process, styrene is distilled under vacuum, and the partial pressure of oxygen is too low to make these inhibitors effective. Both are used in storage applications, in concentrations of 10-100 ppm, depending on temperature and storage time. TBC is generally preferred.

In the distillation section, sulfur and sulfur dioxide have been used as polymerization inhibitors. However, a sulfur-containing tar is formed, which presents disposal problems in incineration (high sulfur oxides emissions). Nonsulfur inhibitors have been known for many years, but are more expensive. However, it has been found that styrene recoveries increase with some nonsulfur inhibitors, and that this benefit compensates for the increased cost.

Most nonsulfur inhibitors are nitrogen-substituted aromatics. The effectiveness of nitrophenols increases with the degree of substitution. Phenothiazine has a synergistic effect with phenolics, particularly TBC, in the presence of oxygen. This system works even under partial vacuum, provided some air is injected.

Process Description for Ethylbenzene Dehydrogenation. Fresh ethylbenzene feed, together with recycled ethylbenzene, is vaporized in a heat exchanger by steam and is then mixed with about 10% of the reaction steam before being superheated to 540°C (Fig. A-2, sheet 2).

In the same superheater, the balance of the reactor steam is superheated to 810°C. Boiler feedwater is preheated in an economizer in the convection section of the superheater.

The superheated steam flow is used to reheat reaction products between catalyst beds before joining the superheated ethylbenzene flow. The steam/ethylbenzene mixture enters the reactor at a temperature of 630°C. It passes through two radial-flow catalyst beds, with intermediate indirect reheat by superheated steam.

The crude reactor product contains styrene, hydrogen, unreacted ethylbenzene, benzene, toluene, methane, carbon oxides, and steam. The mix is cooled in the steam boiler, then desuperheated with recycled water before being further cooled by air- and water-cooled condensers.

The condensed reaction mixture separates into three phases: off-gas, organic liquids, and water. The off-gas is compressed and cooled with brine to condense most of the organics, which return to the separator. Part of the aqueous phase is recycled to the desuperheater, and the balance is sent to the condensate stripper (Fig. A-2, sheet 3).

The organic phase is sent to the distillation section, where an inhibitor is added (Fig. A-2, sheet 4).

In the first column, styrene, tars, and inhibitor are separated from the lower-boiling ethylbenzene, toluene, and benzene. These low boilers are separated further in the ethylbenzene column. The mixed benzene/toluene overhead is recycled to the alkylation section, leaving ethylbenzene for recycle to the dehydrogenation section.

The styrene flow from the bottom of the first column is flashed into the styrene finishing column and pure styrene is collected overhead. The bottoms from this column contain tars, styrene polymer, and inhibitor.

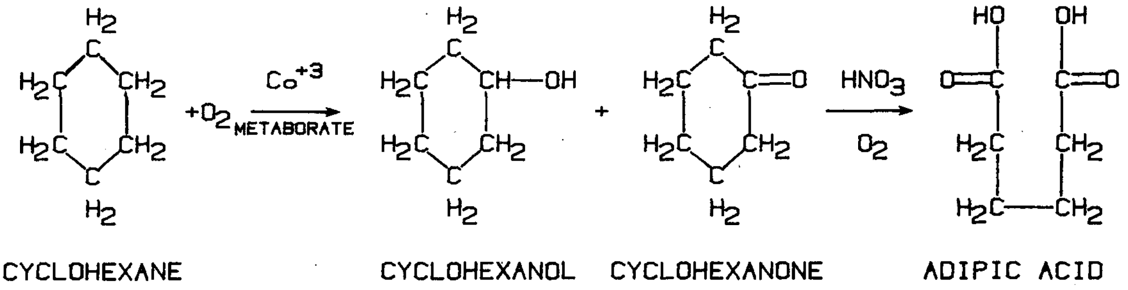
Styrene finishing is temperature-sensitive to polymer formation. Both the primary column and the styrene finishing column operate at reduced head pressures of about 50 mm Hg to maintain bottoms temperatures below about 107°C, reducing polymer formation. The other two columns operate at atmospheric pressure.

A.2.4 Adipic Acid via Cyclohexane Oxidation

A.2.4.1 Process Chemistry

Adipic acid is produced by two-stage, liquid-phase, air and nitric acid oxidation of cyclohexane. The first step gives a mixture of cyclohexanol and cyclohexanone. These are separated from unreacted cyclohexane and further oxidized using concentrated nitric acid. Metaboric acid (20 wt %) is present during the cyclohexane oxidation. This serves to convert cyclohexanol to a metaborate ester, minimizing over-oxidation to maximize yields.

The cyclohexylborate is hydrolyzed, boric acid is recovered, and then cyclohexanol and cyclohexanone are oxidized by nitric acid in a second set of reactors (70°-95°C and 30 psig) to produce adipic acid. Yield is 75% based on moles of cyclohexane. The reaction can be illustrated by the following sequence:



A.2.4.2 Process Design

Figure A-3, sheet 1, is the process flow diagram for the boric acid-air oxidation route to ketone-alcohol from cyclohexane. A series of tank reactors, operated continuously, is used. Air is fed to each stage. Operating conditions are about 350°F and 150 psig pressure. Heat is added through internal coils to boil off the water of reaction. The borate ester of cyclohexanol is formed through addition of metaboric acid. The off-gas, consisting of carbon oxides and nitrogen, is passed first through a partial condenser to recover most of the unreacted cyclohexane, and finally through an absorber-stripper system to complete the recovery.

The borate esters in the outlet from the oxidation reactors are then hydrolyzed back to alcohols and ketones by contact with water in an agitated vessel. After phase separation the cyclohexanol/cyclohexanone mixture is passed on to a scrubbing operation.

Crystallization is used to precipitate boric acid from the water from the phase separator. Centrifugation and drying are used to complete the recovery of boric acid for recycle. The liquid phase from the centrifuge is recycled to the hydrolysis operation.

Organic dibasic acids in the organic layer from the phase separator are extracted with water, which is fed to the adipic acid reactor. Caustic washing is then used on the organic phase to remove acids, another water wash is done, and the neutralized organics go to cyclohexane recovery.

In the cyclohexane recovery column, cyclohexane is taken overhead and returned to the reactors. The residues go to a separation operation. Two towers are needed for adequate recovery of cyclohexane from the ketone/alcohol mixture. The overhead from the second column is mixed cyclohexanol and cyclohexanone.

Figure A-3, sheet 2, shows the nitric acid oxidation of the ketone/alcohol mixture in a two-stage reaction system. The first stage operates at about 165°F, and up to 90% of the organic mixture is converted. Completion of the oxidation in the second stage is accomplished at about 225°F.

Reactor residence time is a function of acid strength and operating temperature, and can be up to two hours. The reactors are sized to divide the residence time equally. Nitric acid to ketone/alcohol ratios can vary between 3 and 6 to one, depending on optimization objectives. Higher ratios improve yields; lower ratios favor lower operating costs. Reactor off-gas is scrubbed with recycle nitric acid to recover entrained acid. Nitrous acid from the reactors is air-oxidized in the scrubber. Vent gases are final-scrubbed before venting to the air.

A crystallization system then takes the crude reaction system product. Two stages are used. The feed to the first stage contains about equal concentrations of adipic acid, nitric acid, and water. There are small, negligible amounts of succinic and glutaric acids.

Ninty-five percent pure adipic acid is produced in the first stage crystallizer. After water dissolution, recrystallization in the second stage yields fiber-grade product. Water-washing is used in both stages.

A rotary dryer accomplishes final water removal, and the dry product is sent to storage and bagging facilities.

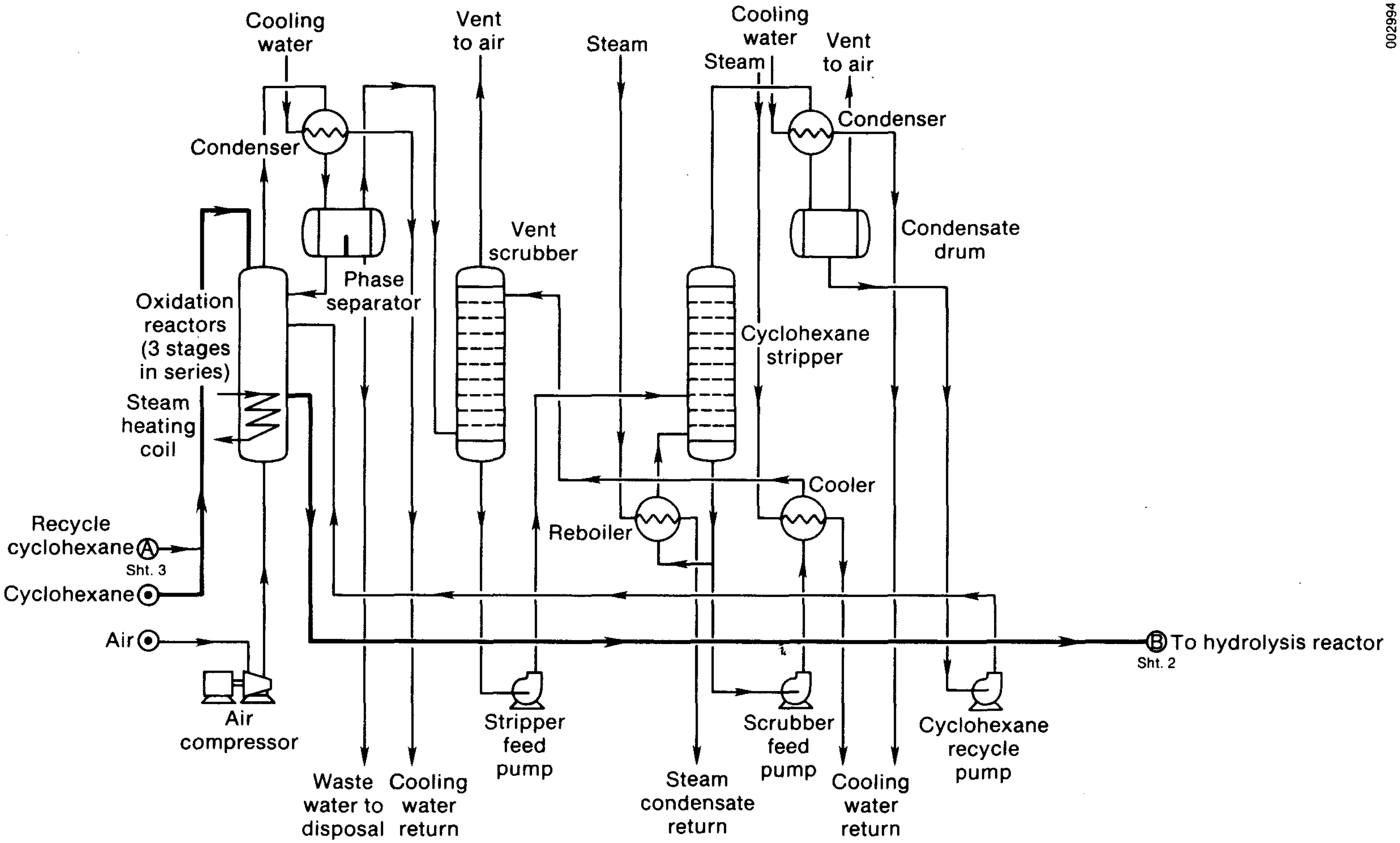


Figure A-3(a). **Process Flow Diagram for Production of Adipic Acid from Cyclohexane** (sheet 1 of 5)

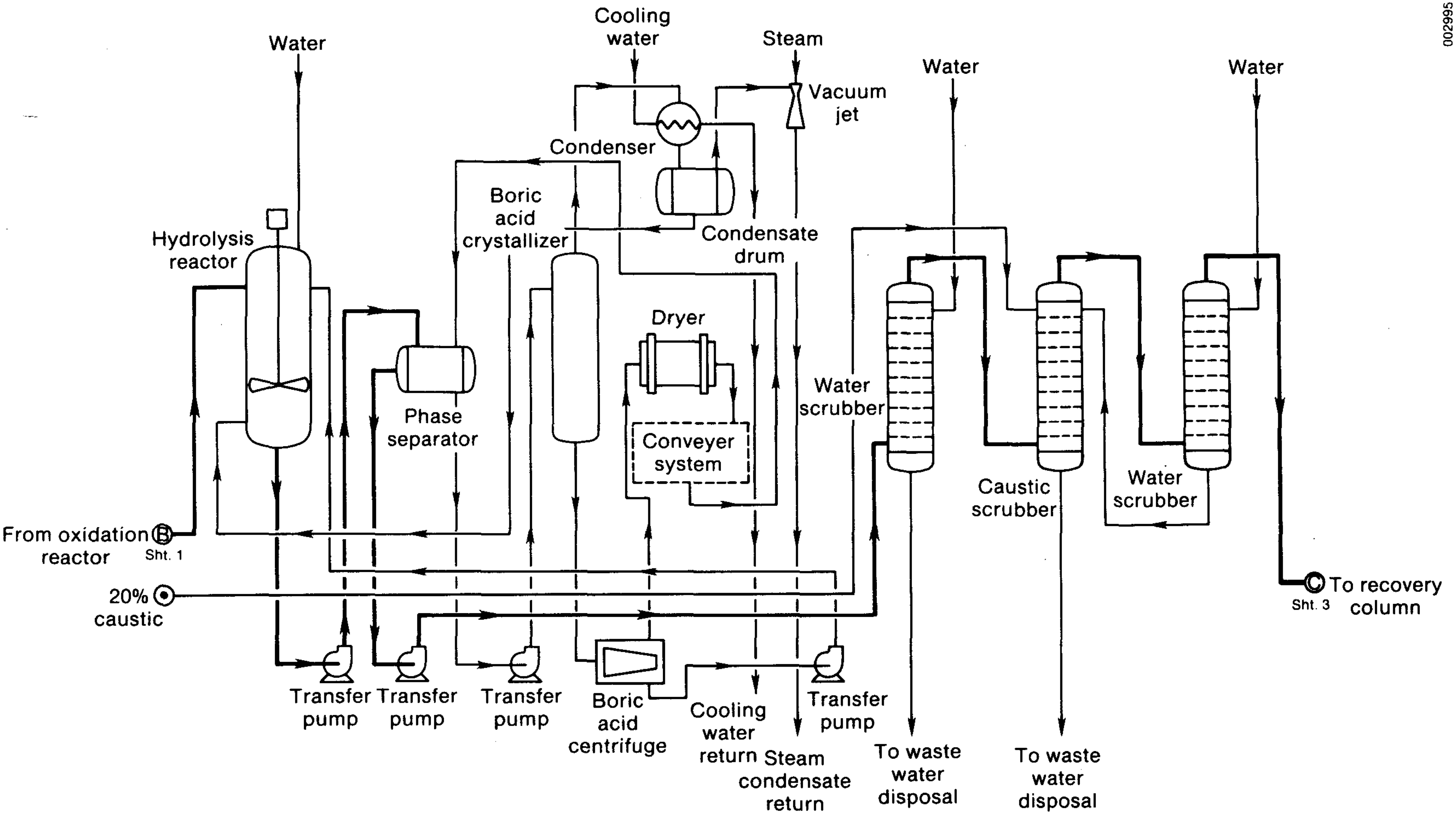


Figure A-3(b). **Process Flow Diagram for Production of Adipic Acid from Cyclohexane** (sheet 2 of 5)

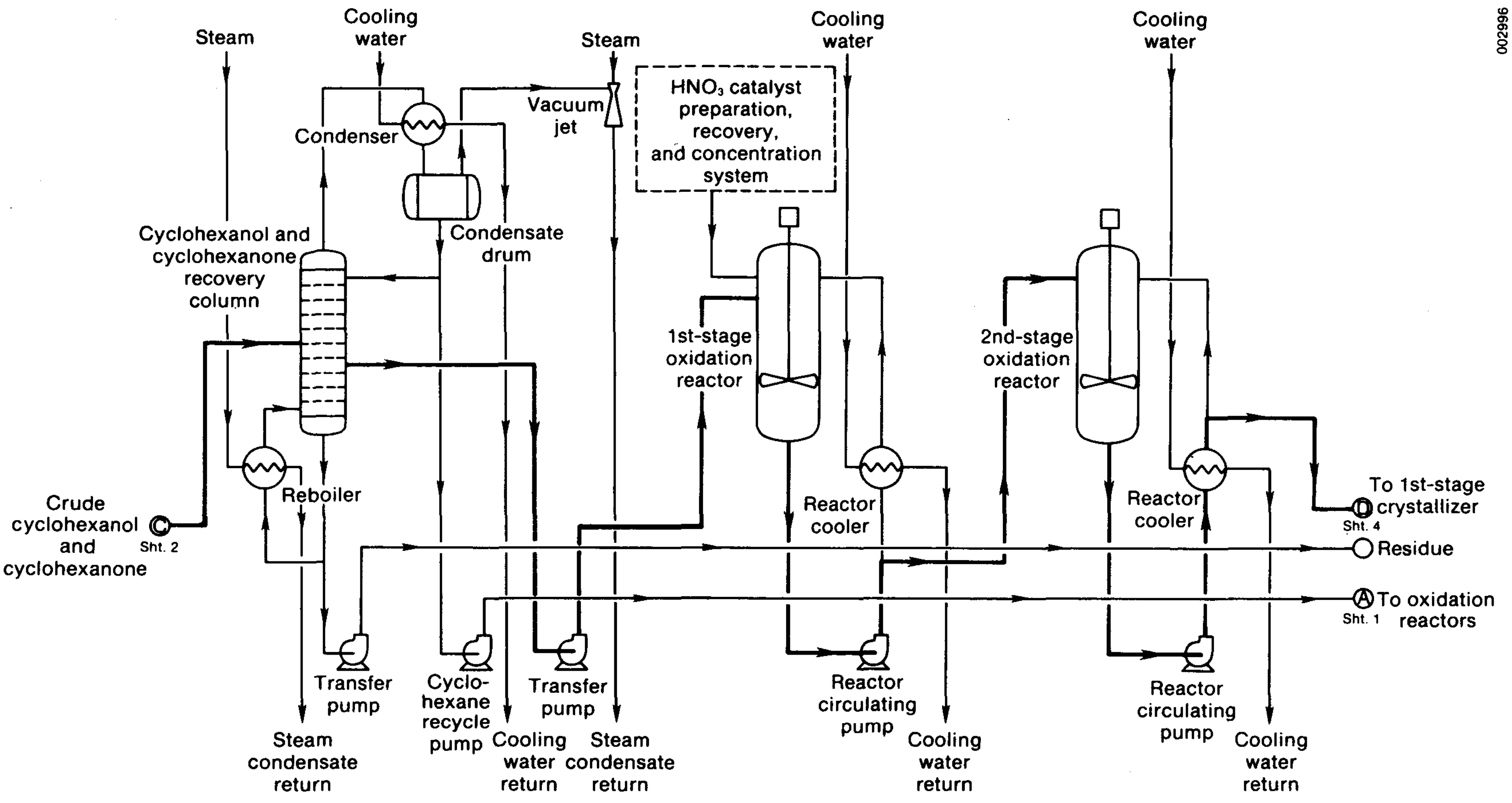


Figure A-3(c). **Process Flow Diagram for Production of Adipic Acid from Cyclohexane** (sheet 3 of 5)

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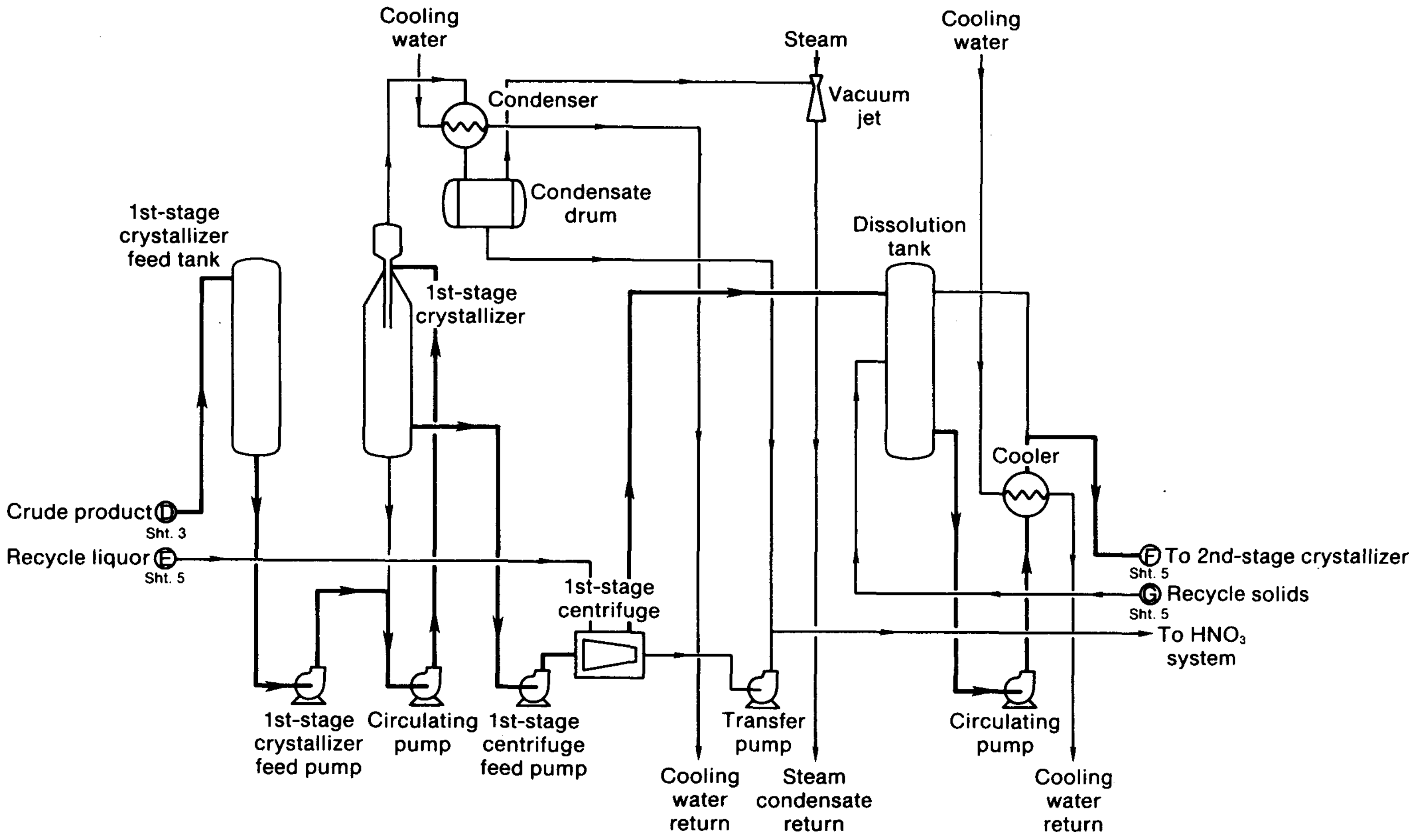


Figure A-3(d). **Process Flow Diagram for Production of Adipic Acid from Cyclohexane (sheet 4 of 5)**

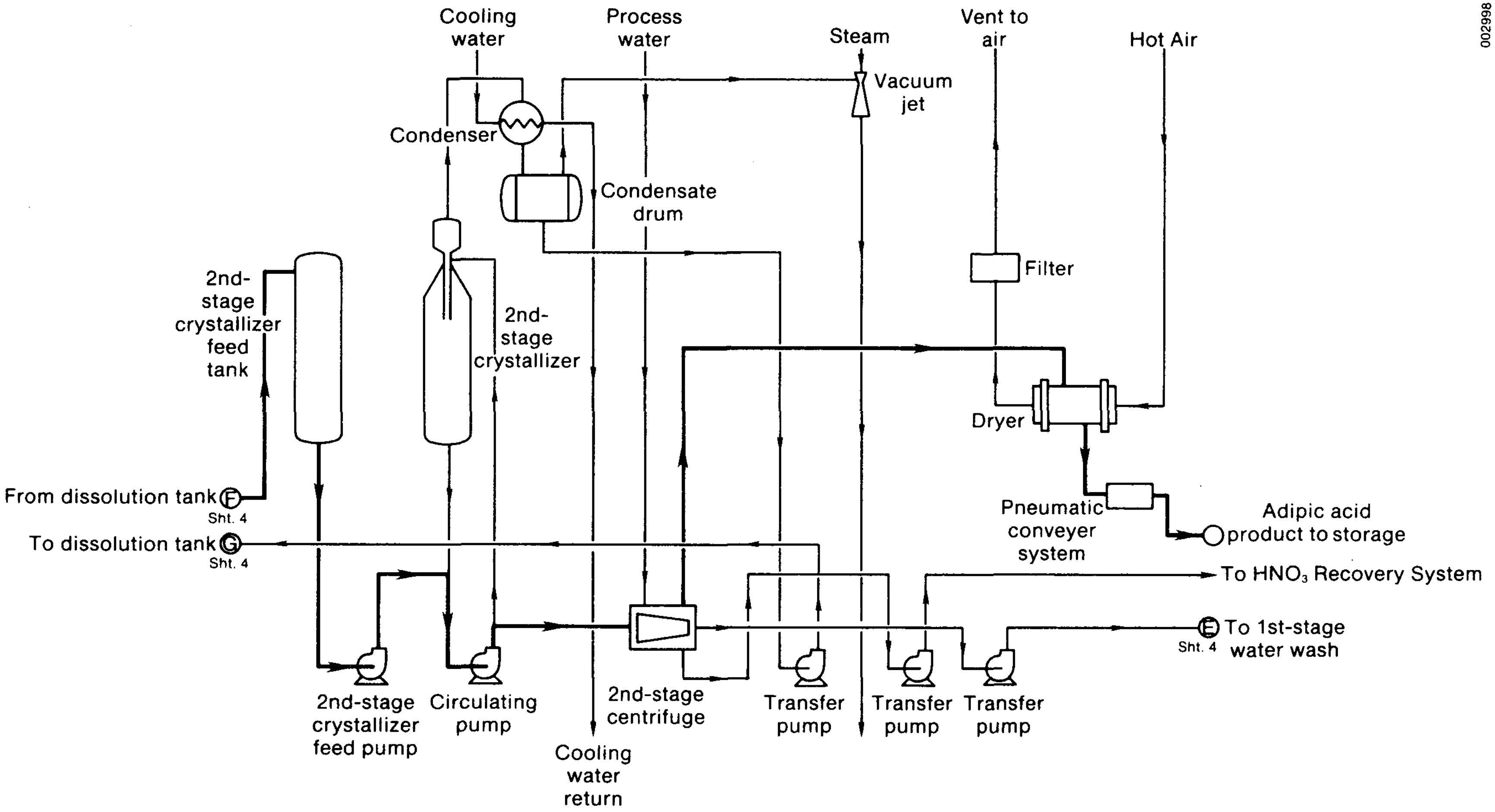


Figure A-3(e). **Process Flow Diagram for Production of Adipic Acid from Cyclohexane** (sheet 5 of 5)

The mother liquor from the crystallizers is combined and fed to a three-tower fractionation system in which 60% nitric acid is recovered from the third tower. The residue from the first tower, water and adipic acid, is recycled to the first stage crystallizer.

A.2.5 Hydrocarbon-Based Technology for Maleic Anhydride

A.2.5.1 Process Chemistry

The difference in price between benzene and n-butane in the United States prompted the development of processes capable of using n-butane as a feedstock for maleic anhydride. Commercial use of the n-butane oxidation to maleic anhydride began in the late 1970s.

The first commercial use of n-butane oxidation to maleic anhydride was by Monsanto (1974,1975), who further developed the vanadium-phosphorus catalyst systems, specifically as systems containing iron. Standard Oil of Ohio, Chem Systems and Amoco, Chevron, Petro-Tex, and Mobil have also published related work.

Some of the butane processes described in the patent literature operated above 450°C and others below this temperature. Companies that have converted existing plants, Monsanto and Petro-Tex, have patented low temperature (400° to 450°C) processes. The only existing grass-roots, butane-based maleic anhydride plant is being operated by Amoco with a high temperature process. The catalyst systems establish the operating parameters. For a relatively simple vanadium-phosphorus composition the temperature would range above 500°C. The catalyst probably deactivates slowly at these high temperatures. Improved compositions allow operation at temperatures between 450° and 500°C. Monsanto and Petro-Tex have disclosed complex compositions that have satisfactory activity at lower temperatures (400° to 450°C). The Monsanto and Petro-Tex catalysts could be used to convert an existing benzene process plant.

An apparent advantage of n-butane technology is that the theoretical yield of maleic anhydride (1.69 lb/lb) is greater than for benzene systems (1.26 lb/lb), because, in effect, two of the six carbon atoms from benzene need not be discarded to synthesize the four-carbon product.

A.2.5.2 Process Design

Monsanto n-butane oxidation technology is the basis of a speculative process design presented in Fig. A-4. The design for a 60×10^6 lb/yr plant is derived from patent disclosures supplemented by engineering judgment. The process consists of three reactors, continuous scrubbing and dehydration, followed by batch refining. Physical properties of maleic anhydride are given in Table A-4.

The feed mixture of air containing 1.5 mol % n-butane enters the reactors after being heated in feed/effluent interchangers. The reactors are multiple packed-tube vessels with cooling provided by circulating molten salt. The operating temperature is 450°C at a pressure of 30 psig. The tubes are packed with a phosphorus/vanadium/iron oxide

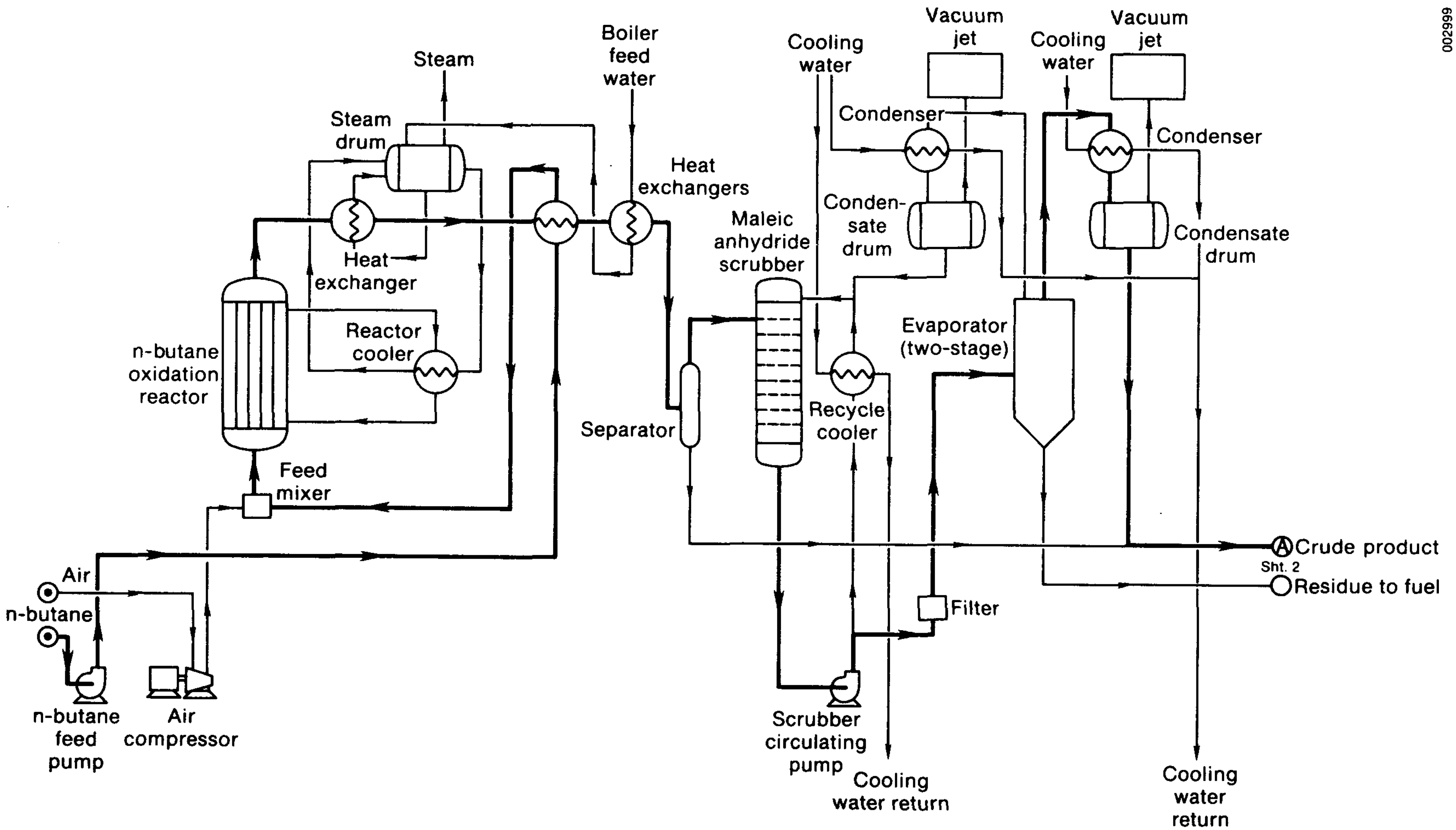


Figure A-4(a). **Process Flow Diagram for Production of Maleic Anhydride from n-Butane** (sheet 1 of 2)

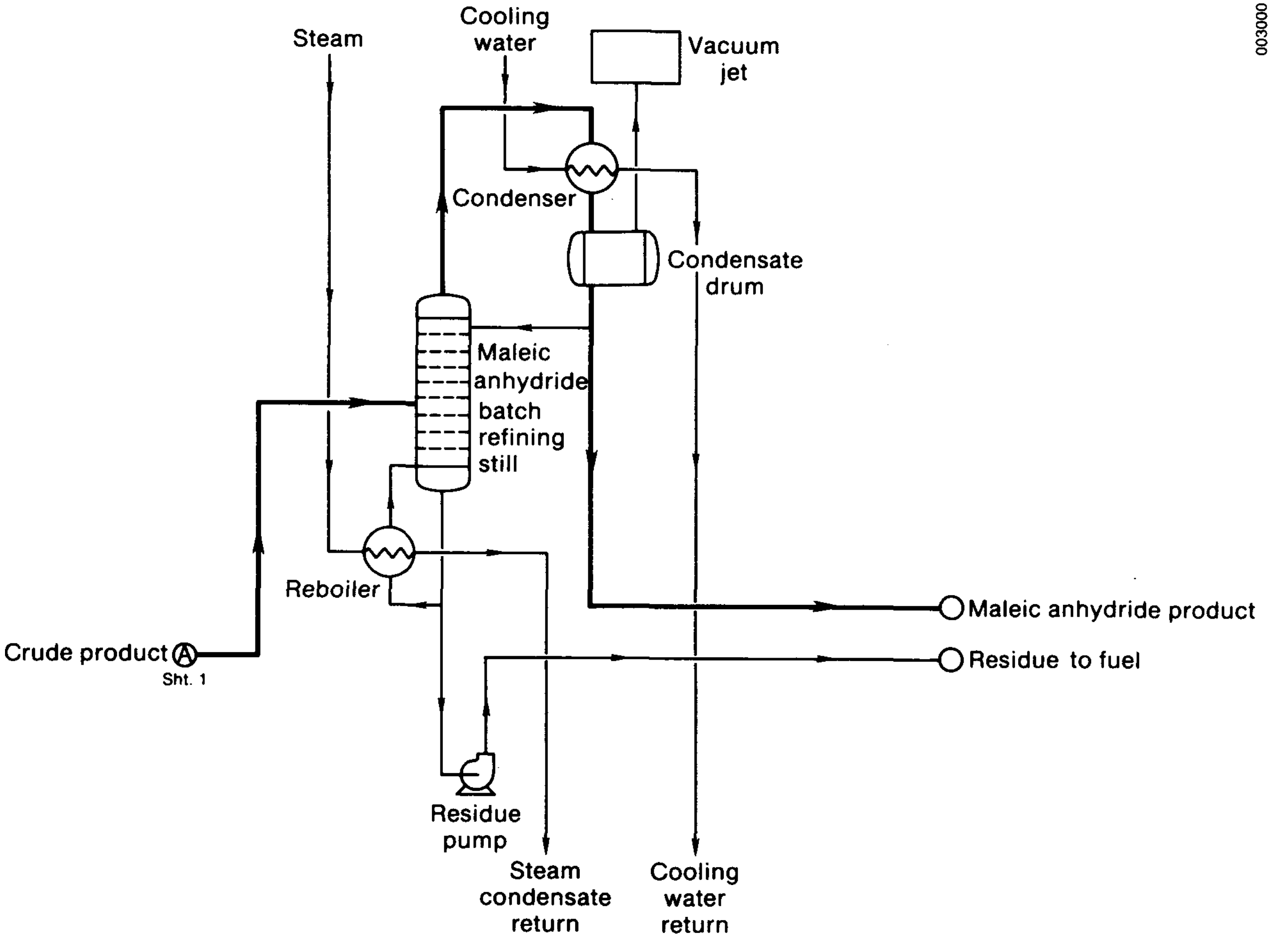


Figure A-4(b). **Process Flow Diagram for Production of Maleic Anhydride from n-Butane** (sheet 2 of 2)

Table A-4. Physical Properties of Maleic Anhydride

Molecular weight	98.06
Specific gravity, 60°C	1.31
Melting point (°C)	57-60
Boiling point (°C)	198
Solubility in water, 30°C (g/100 g)	16.3

catalyst modified by chromium and barium. There is no recycle of unreacted hydrocarbon from the dilute gas. The conversion of 68% of the n-butane with 71% selectivity to maleic anhydride gives an overall yield of 48%.

The product leaving the reactors is cooled in waste heat boilers, the feed/effluent interchanger, and final coolers. The high water content of the reactor effluent limits the temperature to which the product can be cooled. About 30% of the maleic anhydride can be condensed before the dew point of water is reached. Condensed crude maleic anhydride goes to storage and the remaining gases pass into a scrubber. A solution of 35-40 wt % maleic acid scrubs out the remaining maleic anhydride, and the tail gases go to an incinerator for disposal. Recycled water is used for final scrubbing of the tail gases and to maintain the concentration of the circulating maleic acid stream.

Maleic acid solution from the scrubber is filtered; then the concentration of maleic acid is raised to nearly 100% in a thin film evaporator. Operating conditions are 0.4 atm at 125°C. The overhead, mostly water, is condensed and returned to the maleic anhydride scrubber. Concentrated maleic acid (together with some recycled maleic anhydride) is dehydrated in a second evaporator at 140°C and 0.12 atm. The last traces of water are removed in this operation and the maleic acid is converted to maleic anhydride. Tarry residues from the evaporator go to the incinerator for disposal. Maleic anhydride overhead is partially condensed in a tempered water exchanger and goes to a refining column for final purification. A cooling water exchanger condenses the remaining anhydride in the overhead from the dehydrator and returns it as reflux. Two parallel trains of concentration and dehydration evaporators are used to allow for downtime for cleaning without interrupting production.

A.3 FURFURAL-BASED ROUTES

The use of furfural as a starting material for the production of n-butanol, adipic acid, maleic anhydride, styrene, and 1,3-butadiene will be discussed in the following subsections. The production of furfural from acid hydrolysis is not described here because it has been described in detail in other SERI reports. The use of furfural as the starting raw material for the synthesis of chemicals assumes that it will be recovered in satisfactory purity from the acid hydrolysis and prehydrolysis effluent streams. This will probably involve fractionation of the flash tank condensate.

The process chemistry for converting furfural to derivatives of commercial interest is largely speculative. For some it is first necessary to convert the furfural by decarboxylation to furan, then by hydrogenation to tetrahydrofuran (THF). Tetrahydrofuran can be converted using oxo chemistry to adipic acid via a route documented by German workers (BIOS 1948).

By analogy to existing technology for the oxidation of n-butane, furan or THF would be a logical candidate for oxidation via a similar catalytic process to form maleic anhydride. The MITRE report (Johnson 1983) cites a personal communication with a member of the technical staff at Quaker Oats indicating that direct catalytic, vapor-phase oxidation of furfural gives nearly quantitative yields of maleic anhydride. This alternative would be simpler and more desirable as a route to maleic anhydride from furfural.

Furan is the starting material for the production of n-butanol. It appears relatively straightforward to catalytically open the ring and add hydrogen in the vapor phase. An alternative route to n-butanol would involve the chemistry developed by Cass of DuPont (1940, 1945). In this invention, THF is converted in an acid-catalyzed, liquid-phase reaction to a dihalogenated, linear, four-carbon compound, e.g., 1,4-dichlorobutane. This should be readily converted either to n-butanol or to 1,3-butadiene by analogs of well-established chemistry. The documented speculative route to 1,3-butadiene proceeds from THF in a vapor-phase dehydration process.

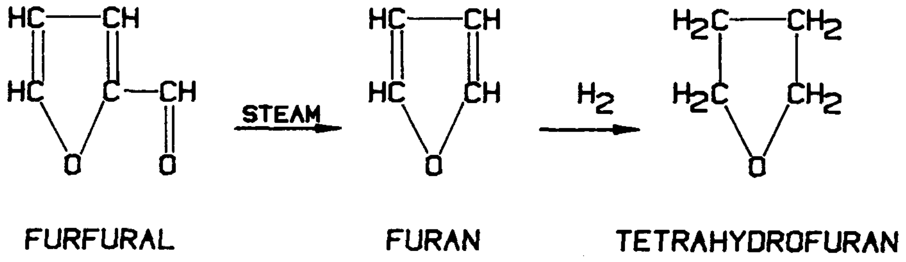
The production of furan and tetrahydrofuran are presented first; the speculative routes to the other derivatives of commercial interest follow. In addition to process descriptions, speculative costs of production are estimated for each derivative. These are used with the product price estimates via hydrocarbon-based technology (preceding section) to establish a net value for the furfural derivatives, THF, and furan. This procedure shows which routes have commercial potential without the need to establish a by-product value for furfural in the context of ethanol production.

A.3.1 Furan and Tetrahydrofuran from Furfural

A.3.1.1 Process Chemistry

The production of furan from furfural has been shown to proceed via catalytic removal of the aldehyde side chain. The reaction is carried out at 400°C over a catalyst of mixed zinc chromite and either manganese or iron (DuPont 1940, 1945). Selectivity to furan is quite high and the overall yield from this step appears to be commercially satisfactory.

The hydrogenation of furan to tetrahydrofuran (THF) can probably be carried out in the vapor phase with a large excess of hydrogen over conventional nickel-based hydrogenation catalysts.



A.3.1.2 Process Description

Vaporized furfural and steam are passed into a vertical furan reactor, where they contact a zinc-chromium-molybdenum catalyst. Exit vapors from the reactor first pass through a water-cooled, partial condenser, then a refrigerated condenser operating at 0° C, to condense the furan. Uncondensed gases consist chiefly of carbon oxides and hydrogen. These are used for fuel or the hydrogen may be recovered for use in the THF synthesis. Condensate is distilled and then hydrogenated under pressure in contact with a nickel-based hydrogenation catalyst. Conversion to tetrahydrofuran is nearly complete. A final distillation produces high-purity tetrahydrofuran (see Figure A-5).

A.3.2 Normal Butanol from Furan

A.3.2.1 Process Chemistry

n-butanol can be produced directly from furan dissolved in acetic acid and dioxan by hydrogenation in the presence of a suitable catalyst (ICI 1947). The cited example of continuous hydrogenation uses a catalyst composed of copper and zinc carbonates in a 1 to 2 molar ratio. A mixture of hydrogen and furan is passed over this catalyst at a pressure of 250 atmospheres at 300° C. The space velocity of the furan is about 0.25 h^{-1} on a liquid volume basis. The ratio of hydrogen to furan in the vapor is about 16 to 1. The product gases contain about 5% unreacted furan, 60% normal butanol, and 35% tetrahydrofuran. The tetrahydrofuran can be recovered as a by-product of value.

A.3.2.2 Process Description

The furan is preheated and vaporized into the hot, compressed hydrogen stream. The hot vapors pass over the copper-zinc catalyst in a packed bed reactor at 300° C with an inlet pressure of 250 atm. The vapors exiting the reactor are quenched in a partial condenser and used to raise some low-pressure steam for use in the process. The butanol and part of the THF by-product condense and are removed. The hydrogen stream is cooled further in a refrigerated condenser (0° C) to remove the remaining THF and butanol. It is then compressed and reheated for recycle to the reactor. The condensed liquids are separated by distillation. The THF is more volatile and is separated overhead in the first column. The n-butanol-water azeotrope is taken as a vapor product in the second column and the water of reaction is removed from the azeotrope in the third column to produce the finished product. The speculative process is shown in Figure A-6.

A.3.3 Butadiene from Tetrahydrofuran

A.3.3.1 Process Chemistry

Work has been reported that shows very high yields of butadiene from tetrahydrofuran over an acid phosphate catalyst (I.G. Farben 1939). At a temperature of about 300° C, 65% conversion per pass of the tetrahydrofuran was obtained over a mixed catalyst of fused sodium orthophosphate, orthophosphoric acid, and nickel acetate. The reaction vapor contains 97% to 99% butadiene among the reaction products. The remaining unconverted THF can be recycled to the process. An inert gas diluent is suggested in the patent and incorporated in the process description which follows.

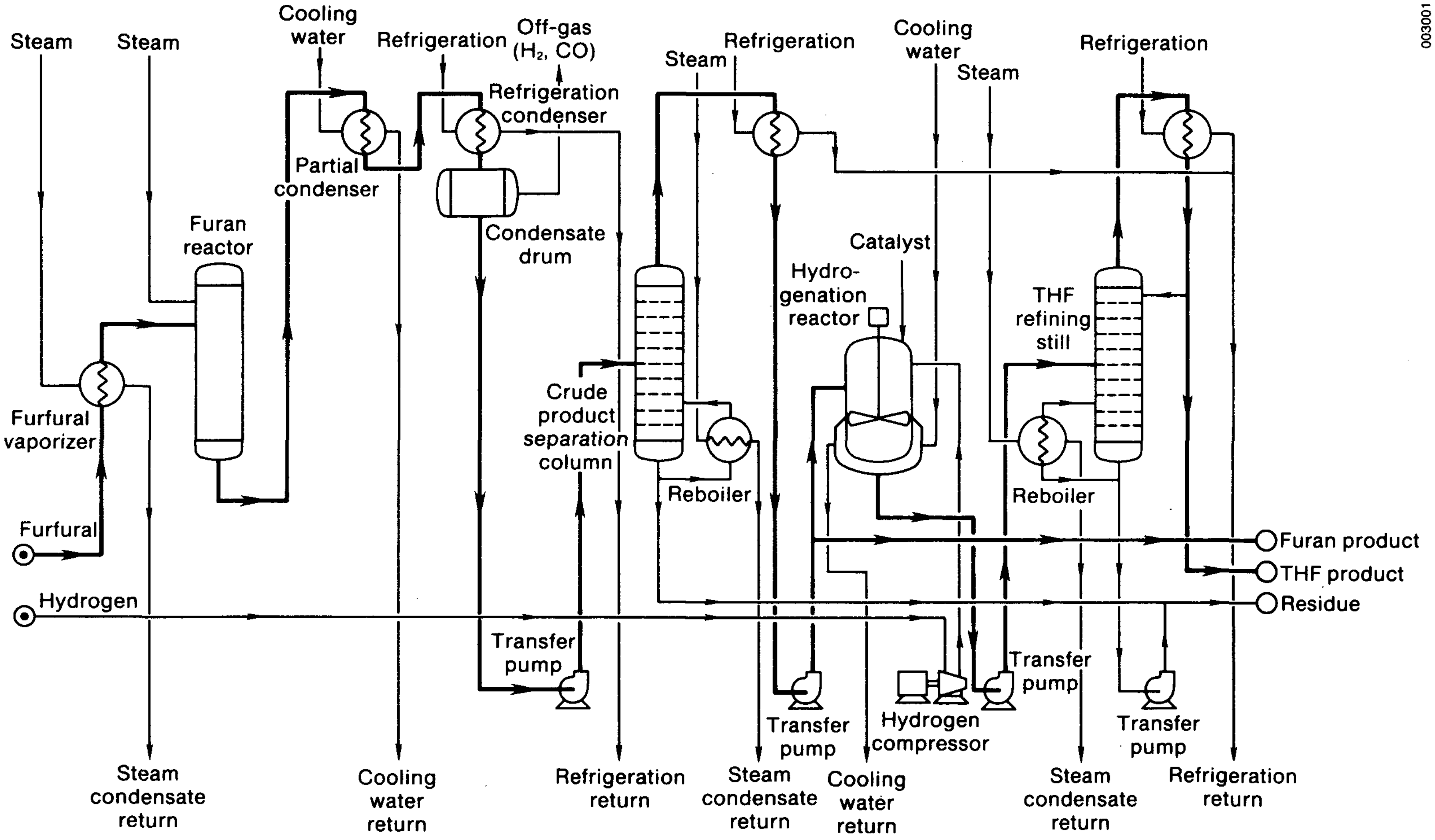


Figure A-5. Process Flow Diagram for Production of Furan and Tetrahydrofuran from Furfural

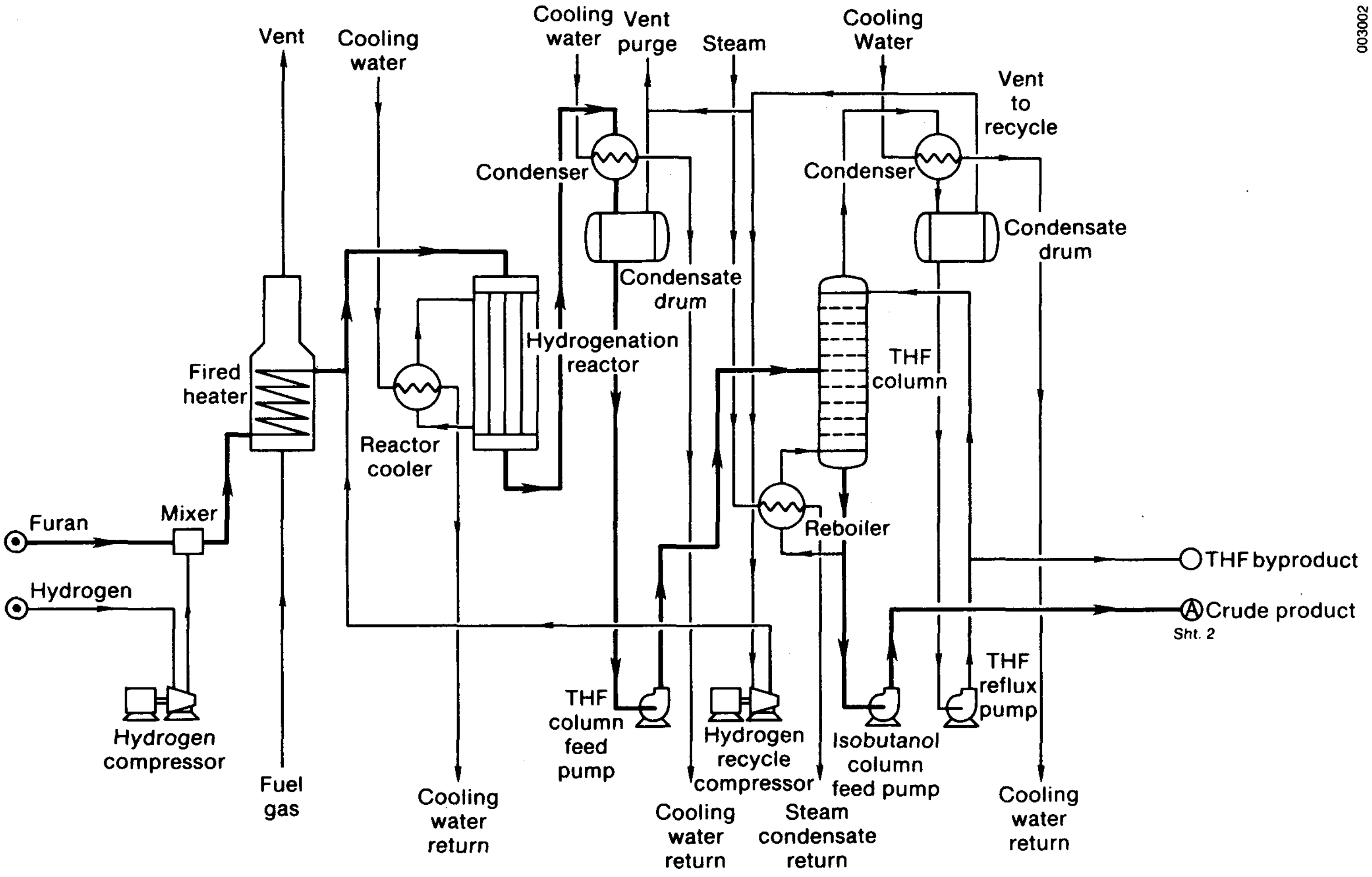


Figure A-6(a). **Process Flow Diagram for Production of n-Butanol from Furan** (sheet 1 of 2)

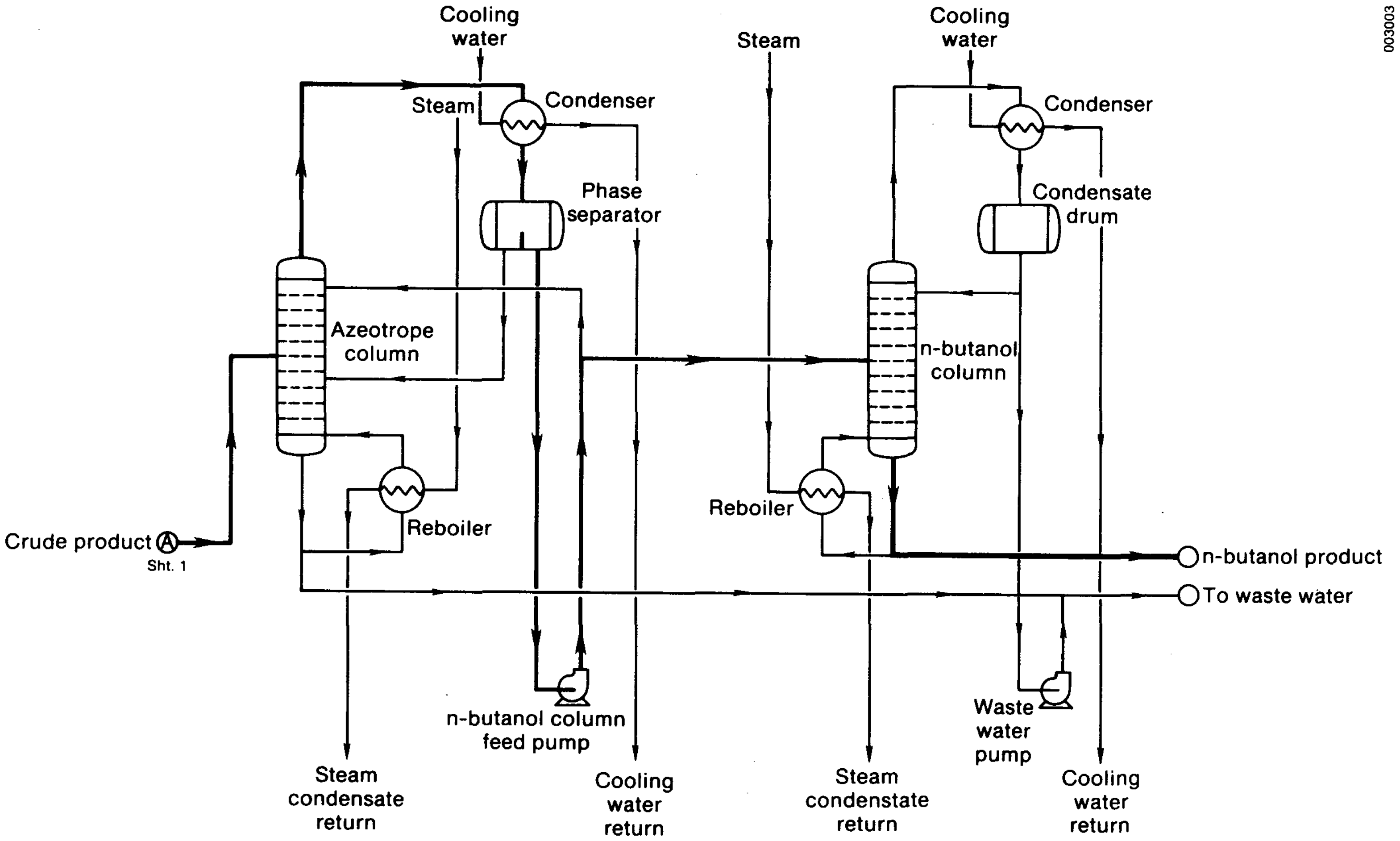


Figure A-6(b). **Process Flow Diagram for Production of n-Butanol from Furan** (sheet 2 of 2)

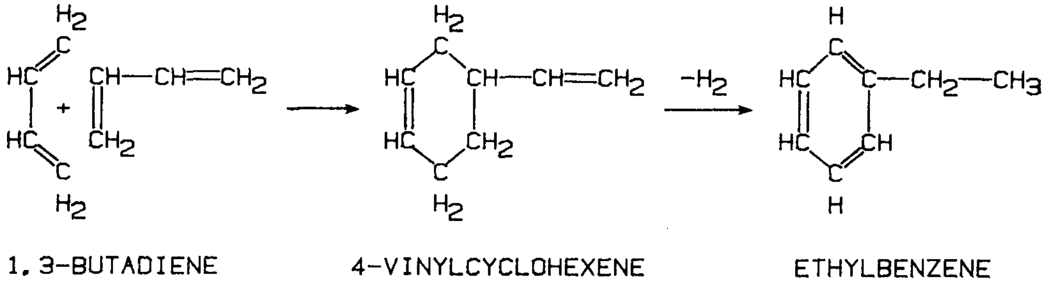
A.3.3.2 Process Description

THF is heated and vaporized into an inert gas stream which is then heated to 310°C and passed through a packed-bed reactor containing the acid phosphate catalyst. The catalyst is a mixed fused product of sodium orthophosphate, phosphoric acid, and nickel acetate. The reactor is operated at a 310°C inlet temperature, an inlet pressure of 50 psig, and a gas-to-catalyst space velocity of 20 h^{-1}. Product gases from the reactor are cooled, first to raise some low-pressure steam, then with air and cold water to condense the THF for recycle. The butadiene passes through low-temperature fractionation to produce a polymer-grade product (see Figure A-7).

A.3.4 Styrene via Butadiene Dimerization

A.3.4.1 Process Chemistry

The application of the Diels-Alder reaction presents a potential commercial route for converting butadiene to ethylbenzene or styrene. The key intermediate is 4-vinylcyclohexene-1 (VCH):



This intermediate can then be dehydrogenated to ethylbenzene or, under more severe conditions, oxidatively dehydrogenated directly to styrene. The production of VCH is not currently practiced commercially for economic reasons, rather than because of technical difficulties; its synthesis from butadiene can be effected almost quantitatively and its separation is not difficult.

The most promising approach to the synthesis of VCH uses a low-temperature, soluble organometallic catalyst. The process operates at 0-80°C and 15-200 psi. Some examples of the catalysts employed are shown in Table A-5.

Selectivities approaching 100% at complete (100%) conversion have been obtained at residence times of 0.5 to 5.0 h. Furthermore, operation with dilute butadiene streams (a hydrotreated steam cracker C_4 stream, for example) gives similar yields.

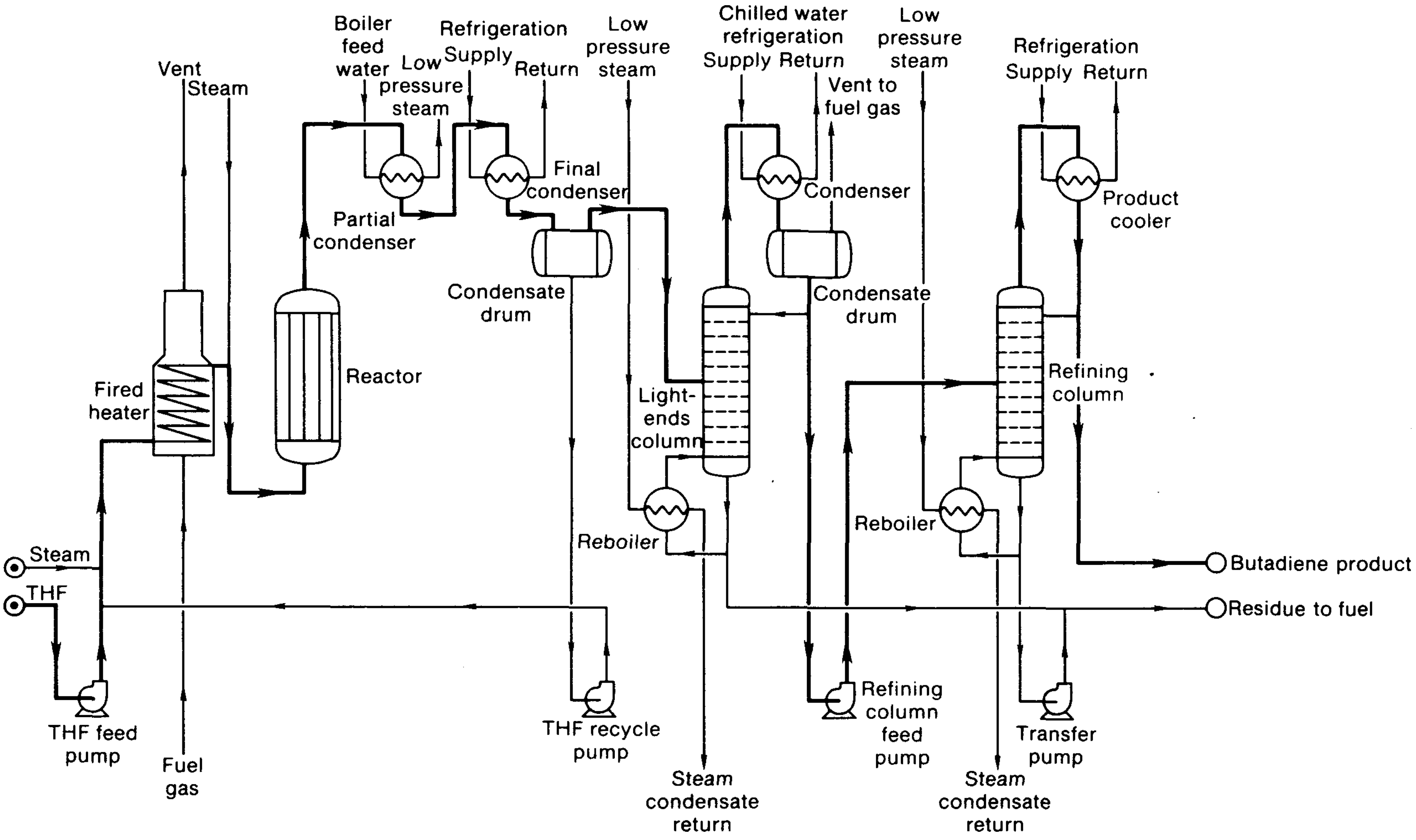


Figure A-7. Process Flow Diagram for Production of 1,3-Butadiene from Tetrahydrofuran

Table A-5. Butadiene Dimerization Catalysts

Company	Catalyst
Elf Aquitaine	$NaFe(CO)_3NO + Ni(CO)_2Br$
Institute Francais du Petrole	$NaFe(CO)_3NO + ZnCl_2$
Phillips	$(C_3H_5)(NO)_2Fe_2SnCl_2$
Societe Chimique des Charbonnages	$Fe(NO)_2Cl$ + Ni(1,5-cyclooctadiene)

Two patents report a high yield of ethylbenzene from VCH by vapor-phase catalytic dehydrogenation. The first of these (BASF 1975) describes the cofeeding of hydrogen and VCH in molar ratios of 10 to 30 at 8 atm pressure, 400-420° C, and liquid hourly space velocities of 1 to 2.5 h^{-1}. Complete conversion in one pass of VCH is obtained with yields to ethylbenzene of 90.5%-96.6%. Noble metal catalysts, such as 0.6% platinum on gamma-alumina or rhenium on alumina, give better results than cobalt-molybdenum catalysts. The purpose of the hydrogen feed is to keep the catalyst free of coke. Months of operation between catalyst regenerations are claimed. Conditions are chosen to minimize hydrogenation of ethylbenzene.

Xylenes must be removed from the product so that they do not affect the purity of the final styrene. Since ethylcyclohexene is a styrene precursor, it can be carried along with the ethylbenzene. The ultimate yield then increases to 97.8%.

The second patent (ARCO 1977) claims the use of potassium oxide-promoted cobalt molybdate on alumina catalyst. ARCO cofeeds inert gas (e.g., steam, CO_2, or N_2), rather than hydrogen, with the VCH. Temperatures of about 400° C at atmospheric pressure are used, and the liquid hourly space velocity is about 1 h^{-1}. Conversion of the VCH is complete, and yields of ethylbenzene are in the range of 90%-92%.

This patent by ARCO is interesting because it might be directly linked with a second-stage conventional styrene dehydrogenation reactor to, in effect, directly convert VCH to styrene. A potential problem with this linkage is xylene by-product contamination of the styrene.

A.3.4.2 Process Description

Considering the state of the art, butadiene to ethylbenzene is the most reasonable choice for a furfural-based alternative. A representative process flow diagram is presented in Figure A-8.

The butadiene stream is combined with a VCH solution of an iron nitrosyl halide organometallic catalyst and fed to a non-back-mixed reactor at 60° C and 10 atm. Patent data show a butadiene to iron molar ratio of 1000. Complete conversion to VCH should occur in less than one hour. The reaction products pass into the depentanizer column, which removes all the compounds boiling below VCH (128.9° C).

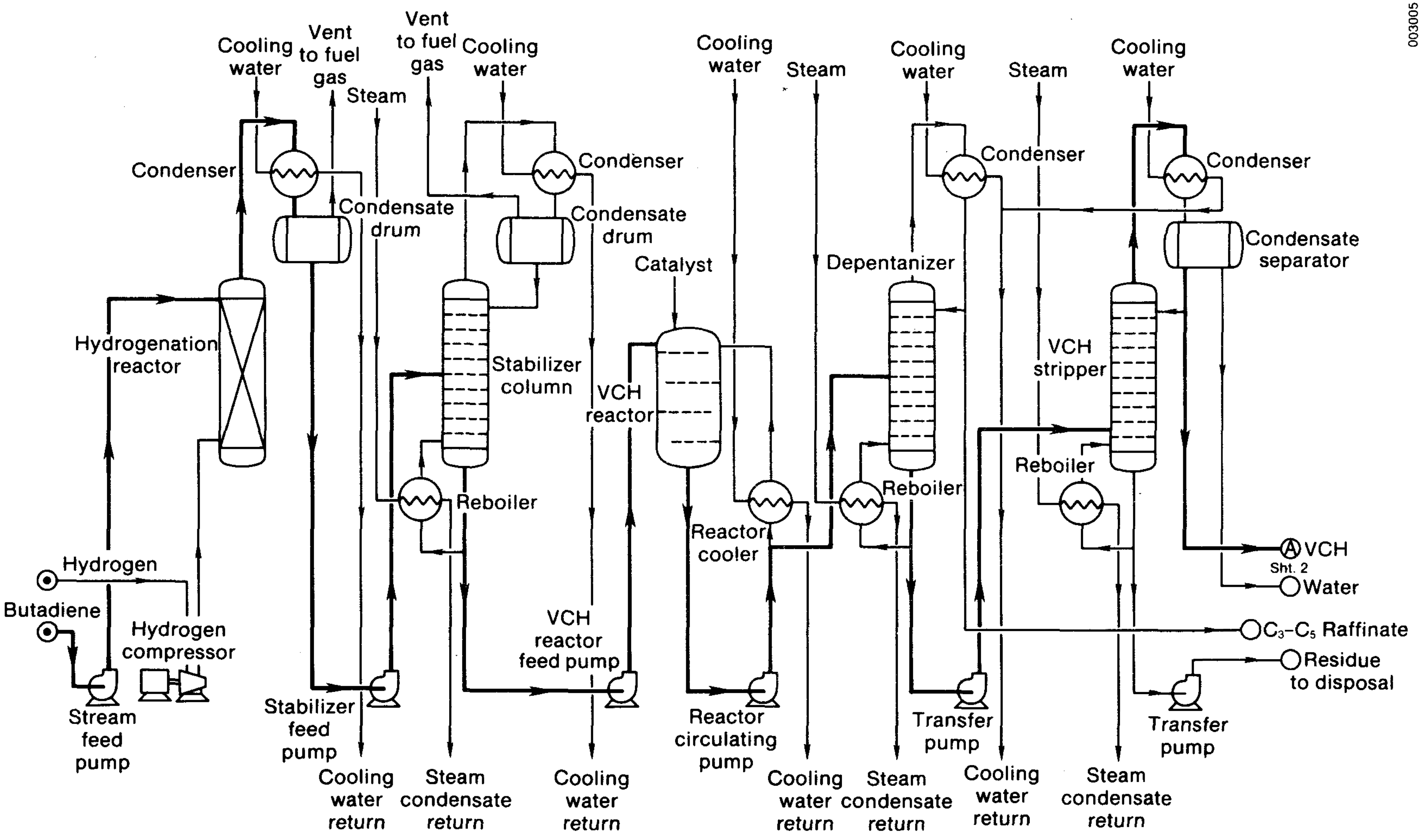
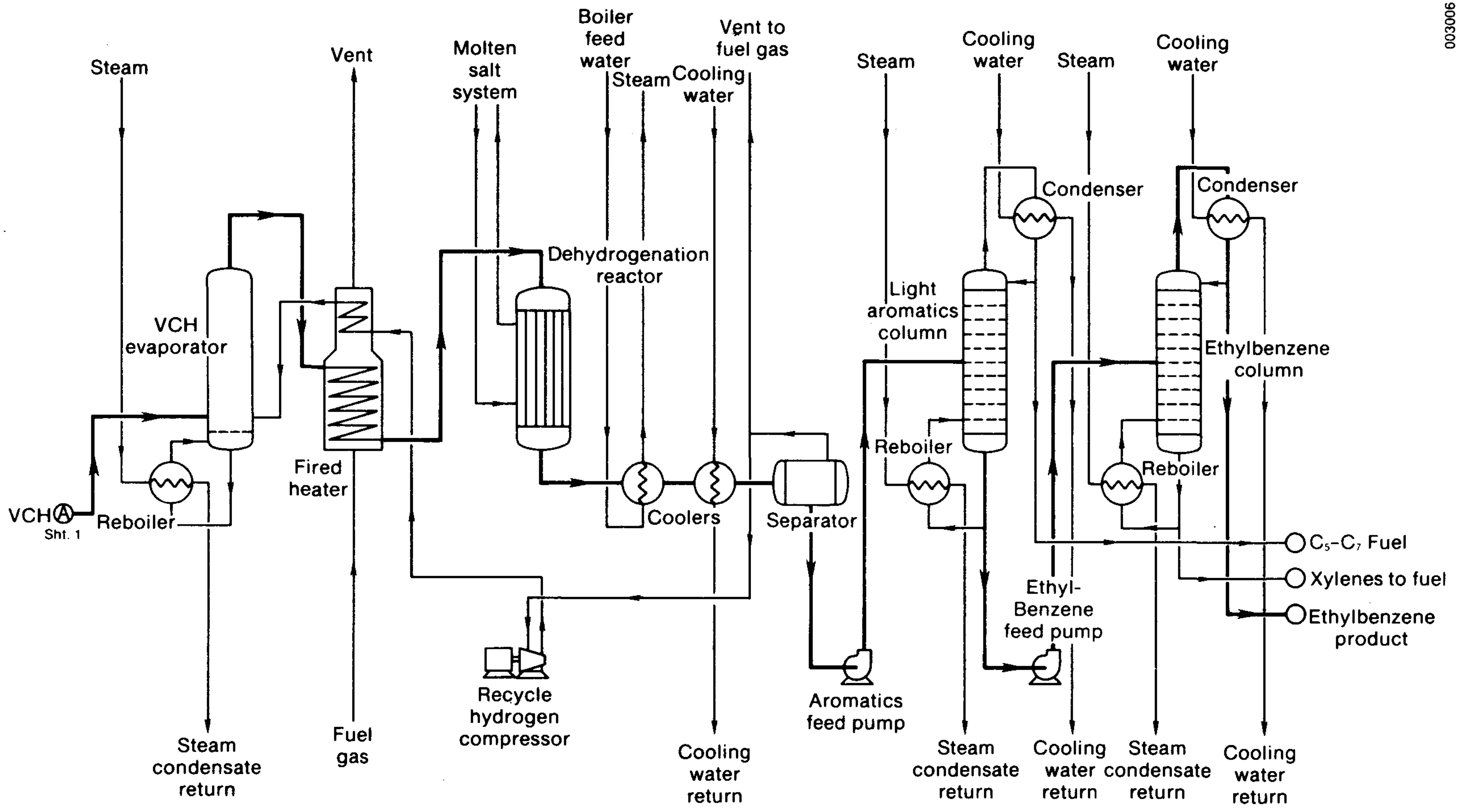


Figure A-8(a). **Process Flow Diagram for Production of Ethylbenzene from Butadiene (sheet 1 of 2)**



Note: Ethylbenzene converted to styrene by dehydrogenation as shown in Figure A-2 sheets 2 through 4.

Figure A-8(b). **Process Flow Diagram for Production of Ethylbenzene from Butadiene** (sheet 2 of 2)

This tower operates at 5.5 atm so that cooling water can be employed in the overhead condenser. The bottom stream from the depentanizer goes to the VCH stripper, where direct steam injection is used to reboil the VCH (while simultaneously deactivating the catalyst). This column operates at 8 to 9 atm and requires about 7 mol steam per mol VCH feed. The bottoms contain inactive catalyst, polymer, and carrier VCH.

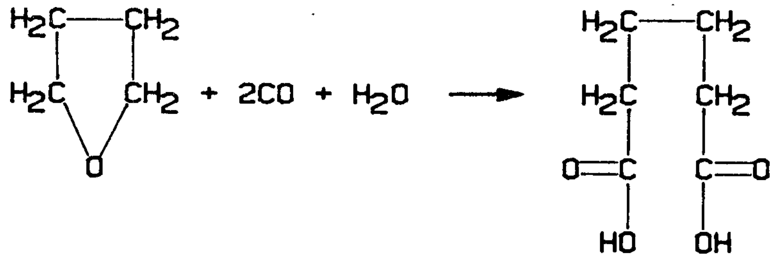
The VCH is evaporated into a stream of hydrogen (10 mol/mol VCH) at 9 atm and passes through a fired heater to preheat it to 315°C. Then the feed enters a multitubular reactor containing 0.6 wt % platinum on gamma-alumina. The endothermic reaction occurs at 400°C with the additional heat provided by a molten salt bath. The VCH liquid hourly space velocity over the catalyst is 2 h^{-1}, and complete conversion of the VCH is obtained with 96.5% selectivity to ethylbenzene. The reactor products are cooled by raising steam, then by cooling water, before passing into a vapor-liquid separator. The exiting hydrogen gas is chilled, and, after the net hydrogen production has been purged to fuel, the gas is recycled by a booster compressor. The liquids are fed to a light aromatics column, which removes the toluene, benzene, and other light hydrocarbons overhead. These are used as fuel. The product stream then passes to the ethylbenzene column, which removes ethylbenzene overhead from xylene and styrene bottoms (which is also sent to fuel).

For the production of styrene (not shown on the process flow diagram), the purified ethylbenzene product is forwarded to a conventional dehydrogenation facility.

A.3.5 Adipic Acid from Tetrahydrofuran

A.3.5.1 Process Chemistry

In an oxo-type reaction, carbon monoxide is added to THF in the presence of nickel carbonyl as a catalyst and nickel iodide as the promoter. The reaction is carried out in the vapor phase at 270°C and 200 atm. The yield is about 80% (BIOS 1948). Under the best laboratory conditions in a stirred autoclave, the yields of adipic acid reached about 75% (Reppe 1953). The liquid-phase reaction under pressure carried out in a column reactor has higher yields, probably due to the closer approach to plug flow conditions.



TETRAHYDROFURAN ADIPIC ACID

A catalyst recovery cycle to capture the nickel and regenerate the nickel carbonyl would also be required. The equations below represent the preparation and recovery (other halides can be substituted for iodine):

$$\mathrm{NiI_2 + 5CO + H_2O} \qquad \mathrm{Ni(CO)_4 + 2HI + CO_2} \qquad \text{(preparation)}$$

$$\mathrm{2\,HI + Ni(CO)_4} \qquad \mathrm{NiI_2 + 4CO + H_2} \qquad \text{(recovery)}$$

The first reaction may be catalyzed by copper and an alternative scheme involves the reaction of copper with nickel iodide to form cuprous iodide and regenerate nickel carbonyl (BIOS 1948).

A.3.5.2 Process Description

A speculative continuous-flow reactor is shown in Figure A-9. A mixture of 93 wt % THF and 7% nickel carbonyl is pumped into the reactor. At the inlet, it is mixed with a solution of nickel and iodide in water at the rate of 1% on THF and recycle condensate of unreacted THF and nickel carbonyl. Carbon monoxide is sparged into the base of the reactor. The working pressure in the reactor is maintained at 200 atm and 270°C. The reactor must be lined with Hastelloy or other highly corrosion-resistant material to resist the acidic iodide solution. The residence time in the reactor is about 10 hours. The design conditions include 90% or more conversion of THF and a 20% conversion of CO. The liquid product from the reactor consists of 80% adipic acid, 5% valerolactone, 15% valeric acid, and the unconverted THF. The gas stream exiting the top of the reactor consists of carbon monoxide saturated with THF, water, and nickel carbonyl. The top of the reactor has a disengagement space and demister to remove entrained droplets. This precaution is especially necessary to limit exposure to highly toxic nickel carbonyl vapor. The gases then enter a flash drum, where the CO is separated for recycle along with make-up gas. A small pilot plant was operated in Germany during the World War II at about 7 liters per day (BIOS 1948). Details of recovery of the product adipic acid and regeneration of the nickel are based on the conventional adipic acid process and on other oxo technology.

The liquid product from the flash drum is cooled and sent to the first-stage crystallizer feed tank. The flashed vapors are compressed for recycle. A purge is scrubbed and incinerated prior to release to the atmosphere. The first stage crystallization produces an adipic acid of about 95% purity after centrifuging. The cake is redissolved and sent to the second-stage feed tank. From the second-stage crystallizer, the product is washed and centrifuged then sent to a dryer and to final product storage. The washing liquors and the mother liquor from the second-stage crystallizer are arranged to maximize counter-current contact with the centrifuge cake. The liquid effluent from the crystallization section is concentrated in a flash column and then recycled to maximize the recovery of adipic acid. Two stages of crystallization with washing of the cake as shown should be sufficient to produce fiber-grade adipic acid.

A.3.6 Maleic Anhydride from Furan

A.3.6.1 Process Chemistry

A speculative route for the production of maleic anhydride from a furfural derivative is based on work done in the mid-1930s (Milas and Walsh 1935). The oxidation of furan was carried out over a vanadium pentoxide catalyst at very high excess air levels. The best yields, about 65% on a molar basis, were obtained with an air-to-furan ratio of 130. The reaction was carried out in the vapor phase at 320°C. The preliminary lab results cited

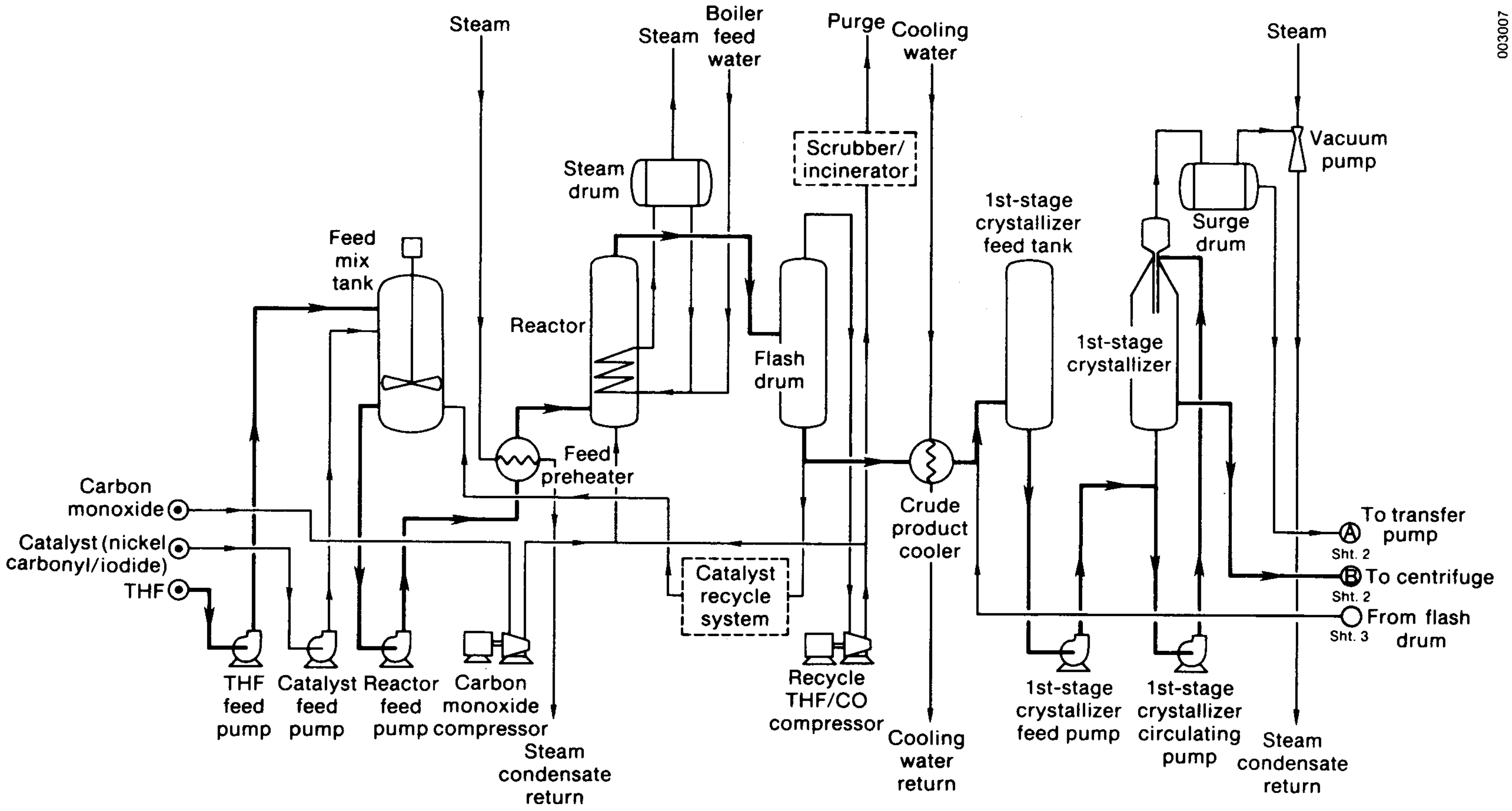


Figure A-9(a). **Process Flow Diagram for Production of Adipic Acid from Tetrahydrofuran (sheet 1 of 3)**

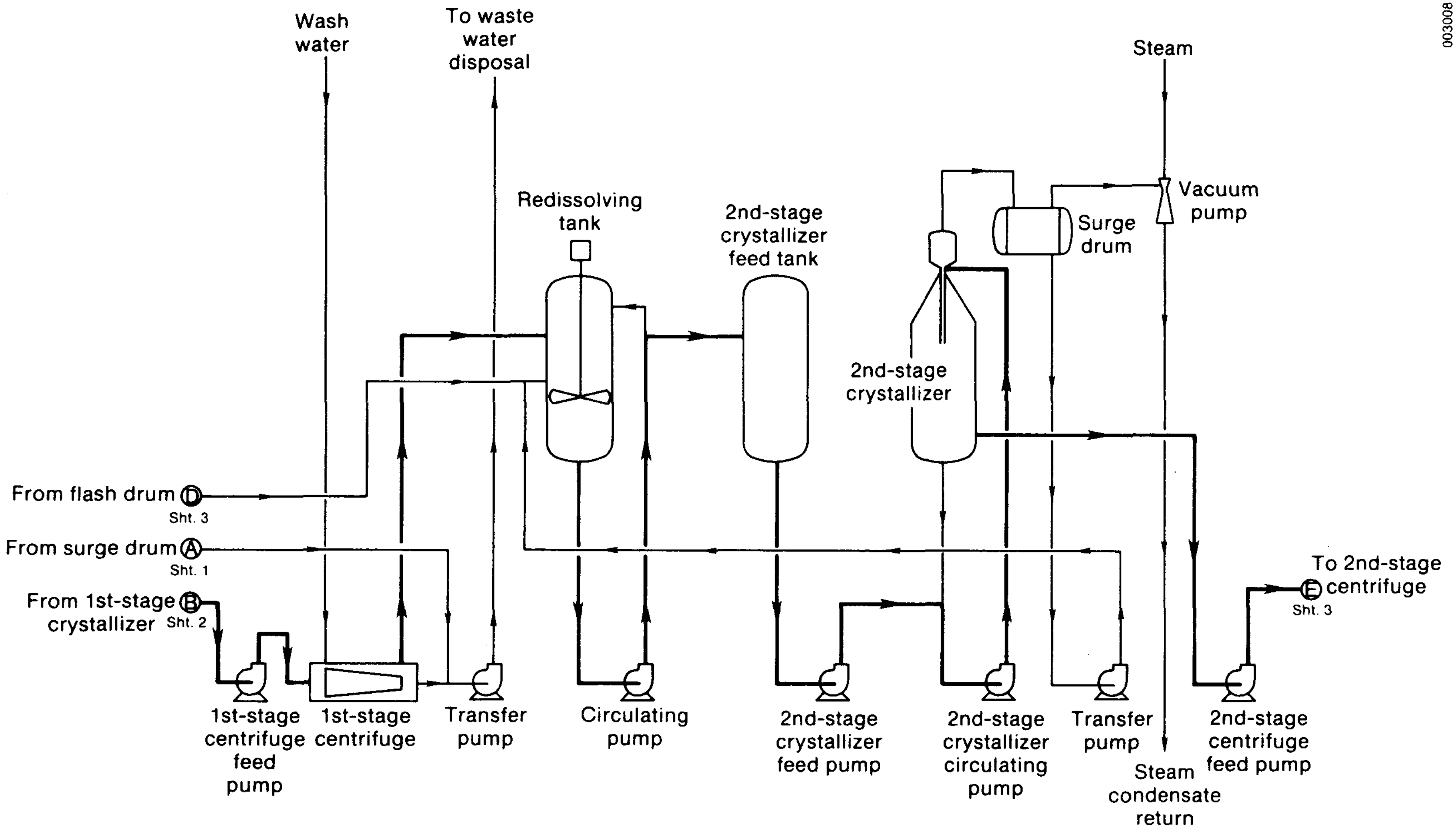


Figure A-9(b). **Process Flow Diagram for Production of Adipic Acid from Tetrahydrofuran** (sheet 2 of 3)

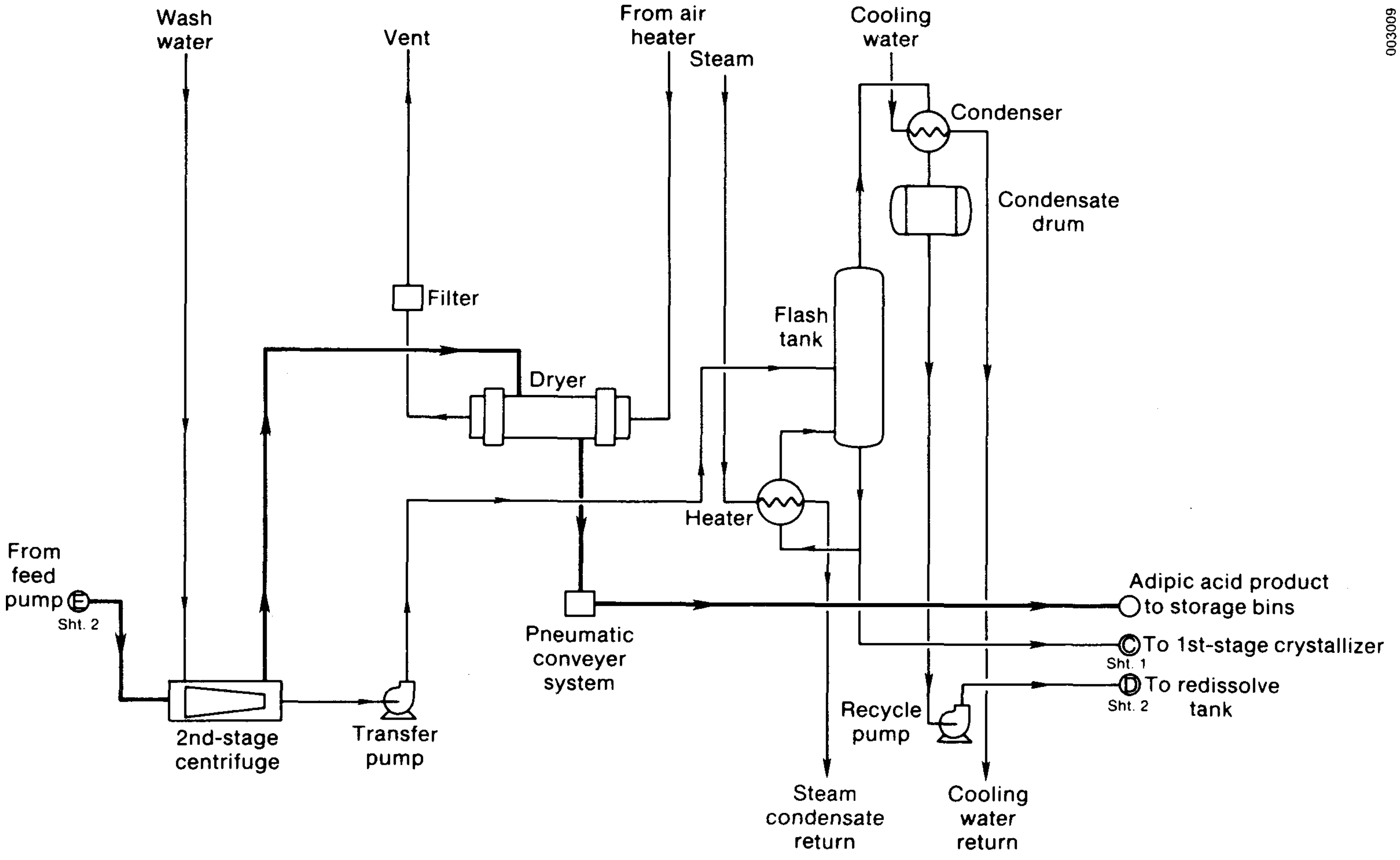
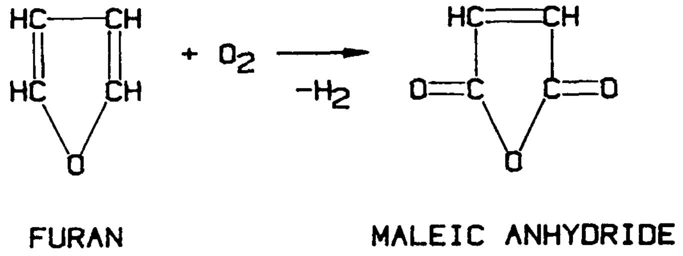


Figure A-9(c). **Process Flow Diagram for Production of Adipic Acid from Tetrahydrofuran** (sheet 3 of 3) were conducted with a feed of about 10 mol of liquid over a period of 4 to 5 hours. The volume of catalyst to feed was not given. There was some minor benefit from the addition of steam to the gas mixture.

For purposes of this speculative process concept, we assume a feed to the reactor consisting of 95 mol % air, 4.44 mol % steam, and 0.56 mol % furan. The reaction is carried out at moderate pressures at 320° C over a vanadium pentoxide catalyst. The catalyst volume is selected so that the furan liquid space velocity is 1 h^{-1}. Complete conversion of the furan occurs with 65% (molar) going to maleic anhydride and 35% going to other products of no value. The maleic anhydride is then recovered by scrubbing the off gases and concentrating and distilling, as in the conventional butane-based process.



A.3.6.2 Process Description

Furan is preheated and vaporized with steam into a hot air stream at a pressure of about 50 psig. The air carries the furan and steam mixture through the reactor packed with vanadium pentoxide on an inert support. The reactor temperature is maintained at about 320° C by the use of a circulating salt bath with an external cooler. The salt cooler is used as a waste-heat boiler to provide part of the steam required in the process. The reactor product gases are scrubbed with water and the off-gases pass through an incinerator before discharge to the atmosphere. The maleic anhydride formed in the reactor is removed from the scrubber, concentrated in evaporators, and then stored in a crude maleic anhydride tank before final distillation to produce the required product. The speculative process concept is shown in Figure A-10.

A.4 PROCESS ECONOMICS

A.4.1 Cost Bases

The capital investments used in this study for estimating the costs of all production routes are lump sums with the usual ±30% uncertainty associated with such estimates. The total fixed investment includes: (1) process (or inside battery limits) plant investment costs; (2) general facilities (or offsites) investment costs; and (3) contingencies. The process plant investment consists of the total cost of all onsite processing units, including all direct and indirect construction costs. No sales or use taxes are included. The capital cost of the offsite facilities includes roads, buildings, railroads, storage tanks, dock, loading and unloading systems, etc. Again no sales or use taxes are included. The project contingency is intended to cover additional equipment that would result from a more detailed design of a definitive project at an actual site.

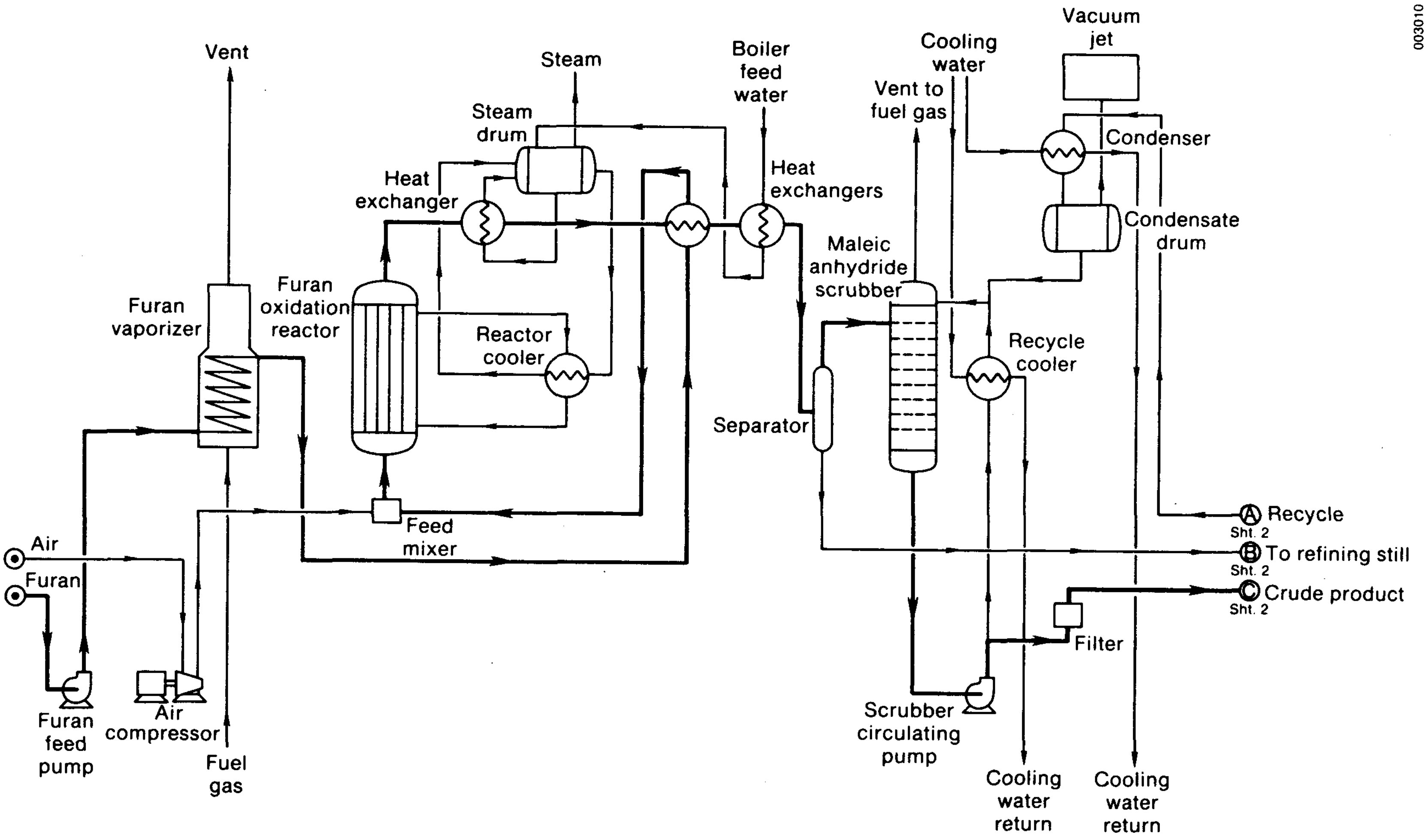


Figure A-10(a). **Process Flow Diagram for Production of Maleic Anhydride from Furan** (sheet 1 of 2)

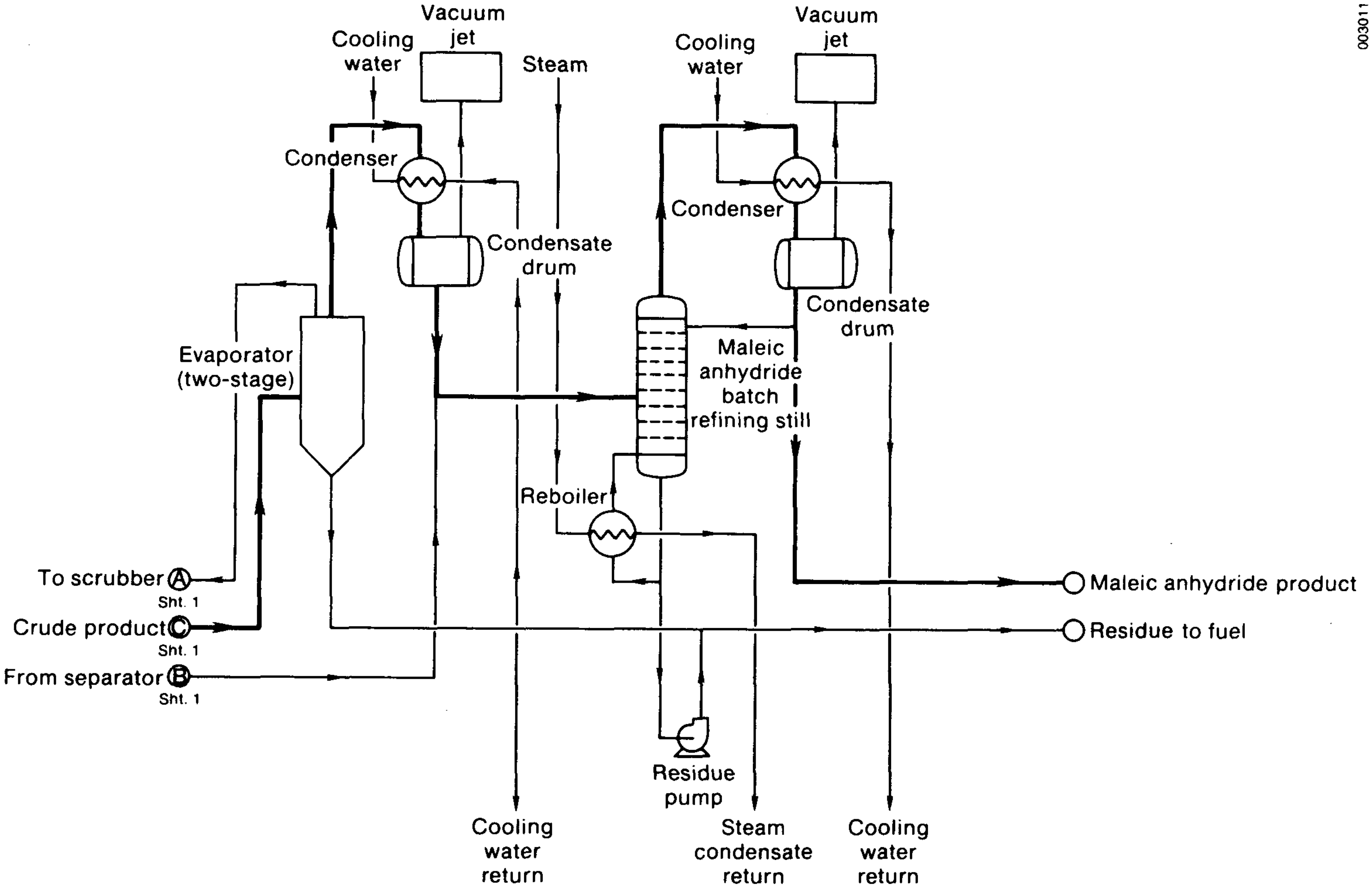


Figure A-10(b). **Process Flow Diagram for Production of Maleic Anhydride from Furan** (sheet 2 of 2)

The discounted cash flow (DCF) analyses in this report contain the following assumptions, unless otherwise stated in the text:

- Time of construction is two years, with uniform expenditure of capital throughout this period
- Working capital is available at completion of construction and is discounted at the same rate as the final DCF percentage. Working capital is recovered at the end of the 10-year life of the project and is calculated as the sum of the first five items minus item six:
    1. Feedstock Inventory—Sixty-day supply of coal and 2-week supply of other raw materials, valued at delivered prices.
    2. Finished Product Inventory—Half month's supply of product, valued at cost of production.
    3. Accounts Receivable—One month's cost of production.
    4. Cash—One week's out-of-pocket expenses, estimated as the cost of production.
    5. Warehouse/Spare Parts Inventory—3 % of inside battery limits capital cost.
    6. Accounts Payable - One month's supply of raw materials at delivered prices.
- Total federal and local taxes are 50%.
- Depreciation is straight line, over five years, with no salvage value for the plant.
- Cost of sales is 10% of the product selling price.
- The sales gradually build up to 60% of capacity in the first year, 80% in the second, and 100% in the third and succeeding years.

The costs of services used to estimate the production costs for the coal slurry fuels are summarized in Table A-6.

Table A-6. Costs of Services (1995 Basis)

Item	Cost
Direct Costs	
Operating factor (h/yr)	8,000
Power ($/kWh)	0.081
Cooling water ($/$10^3$ gal)	0.042
Steam ($/1000 lb)	9.50
Process water ($/$10^3$ gal)	1.35
Foremen ($/yr)	59,000
Operating labor ($/yr)	52,000
Maintenance labor and materials	6% of the inside battery limits capital investment
Indirect Costs	
Overhead	
Direct	45% of labor + supervision
General plant	65% of operating costs
Insurance and taxes	1.5% of total fixed investment
Depreciation	5 year, straight line

Table A-7. Energy and Feedstock Price Forecast for 1995

	Current Price[a]	Projected 1995 Price[b]
OPEC marker crude FOB ($/bbl)	30	67
Average U.S. acquisition ($/bbl)	32	71
Full range naphtha (¢/gal)		
Reformer	83	185
Petrochemical	79	175
No. 2 heating oil (¢/gal)	86	190
Deregulated natural gas ($/$10^6$ Btu)	4	9
Ethane (¢/gal)	37	82
Propane (¢/gal)	52	115
n-butane (¢/gal)	63	140
Benzene (¢/gal)	150	335
Toluene (¢/gal)	110	245
Xylenes (mixed) (¢/gal)	120	265
Ethylene (¢/lb)	26	58
Propylene (chemical grade) (¢/lb)	19	42
Propylene (polymer grade) (¢/lb)		46
Butadiene (¢/lb)	36	80
Butylenes (w/o butadiene) (¢/lb)		34

[a] 1982 $.

[b] 1995 $.

The prices for oil, refined products, and petrochemicals used in these cost estimates are summarized in Table A-7. They are based on price projections for Saudi Light Marker crude that show a decline in real price to 1990 followed by slow growth. The general inflation rate was assumed to be 5% per year in 1983, 6% in 1984, and 6.5% thereafter. Construction costs were assumed to increase by an additional 1% per year.

A.4.2 Cost-of-Production Sheets for Processes

Tables A-8 through A-16 present estimated costs of production in 1995 for the five chemicals considered in this research.

Table A-8. Estimated Cost of Production of n-Butanol via Propylene

Basis: U.S. Gulf Coast in 1995
Capacity: 200 million lb/yr
Operating: 8,000 h/yr

Capital Cost Summary ($ 10^6)

Battery limits	100
Offsites	50
Total fixed investment	150
Working capital	13.82

Production Cost Summary

	Units/lb	Price ($/unit)	Annual Cost ($ 10^3)	$/lb
Raw Materials and By-Products				
Propylene (lb)	0.77	0.42	64,680	
Syn gas (1:1) (10^3 SCF)	0.0126	8.5	21,420	
Hydrogen, (10^3 SCF)	0.0056	12	13,440	
Isobutanol (lb)	-0.11	0.7	-15,400	
Catalyst & chemicals			3,000	
Net Raw Materials Cost			87,140	0.44
Utilities				
Power (kWh)	0.0967	0.081	1,567	
Cooling water (10^3 gal)	0.0083	0.12	199	
Process water (10^3gal)	0	1.35	0	
Fuel (10^6 Btu)	-0.0041	6.5	-5,330	
Steam, 600 psi (10^3 lb)	0.0032	9.5	6,080	
Steam, 150 psi (10^3 lb)	0	9	0	
Steam, 60 psi (10^3 lb)	0	8.9	0	
Inert gas (10^3 SCF)	0.0002	2	80	
Total Utilities Cost			2,596	0.01
Operating Costs				
Operators at $52,000 (4/shift)			957	
Foremen at $59,000 (1/shift)			271	
Supervision at $71,000/yr			0	
Maintenance material and labor (6% of TFI)			6,000	
Total Operating Costs			7,228	0.04
Overhead Expenses				
Direct overhead (45% labor + supervision)			553	
General plant overhead (65% operating costs)			4,698	
Insurance, taxes (1.5% of TFI)			2,250	
Total Overhead Expenses			7,501	0.04
TOTAL COST OF PRODUCTION			104,465	0.52
Depreciation (5 yr, straight line)			30,000	
TOTAL COST PLUS DEPRECIATION			134,465	0.67
SALES PRICE AT 15% DCF				0.88

Table A-9. Estimated Cost of Production of Styrene via Benzene

Basis: U.S. Gulf Coast in 1995
Capacity: 10^9 lb/yr
Operating: 8,000 h/yr

Capital Cost Summary ($ 10^6)

Battery limits	215
Offsites	90
Total fixed investment	305
Working capital	65.25

Production Cost Summary

	Units/lb	Price ($/unit)	Annual Cost ($ 10^3)	$/lb
Raw Materials and By-Products				
Ethylene (lb)	0.2945	0.58	170,810	
Benzene (lb)	0.81	0.44	356,400	
Toluene (lb)	0.0282	0.33	-9,306	
Condensate (lb)	0.0025	0.85	-2,125	
Catalyst & chemicals			11,000	
Net Raw Materials Cost			526,779	0.53
Utilities				
Power (kWh)	0.0316	0.081	2,560	
Cooling water (10^3 gal)	0.019	0.12	2,280	
Process water (10^3gal)	0.00029	1.35	392	
Fuel (10^6 Btu)	0.0033	6.5	21,450	
Steam, 600 psi (10^3 lb)	0.00017	9.5	1,615	
Steam, 150 psi (10^3 lb)	0.00031	9	2,790	
Steam, 60 psi (10^3 lb)	0.00027	8.9	-2,403	
Inert gas (10^3 SCF)	0	2	0	
Total Utilities Cost			28,683	0.03
Operating Costs				
Operators at $52,000 (4/shift)			1,196	
Foremen at $59,000 (1/shift)			271	
Supervision at $71,000/yr			71	
Maintenance material and labor (6% of TFI)			12,900	
Total Operating Costs			14,438	0.01
Overhead Expenses				
Direct overhead (45% labor + supervision)			692	
General plant overhead (65% operating costs)			9,385	
Insurance, taxes (1.5% of TFI)			4,575	
Total Overhead Expenses			14,652	0.01
TOTAL COST OF PRODUCTION			584,553	0.58
Depreciation (5 yr, straight line)			61,000	
TOTAL COST PLUS DEPRECIATION			645,553	0.65
SALES PRICE AT 15% DCF				0.78

Table A-10. Estimated Cost of Production of Adipic Acid via Cyclohexane

Basis: U.S. Gulf Coast in 1995
Capacity: 200 million lb/yr
Operating: 8,000 h/yr

Capital Cost Summary ($ 10^6)

Battery limits	110
Offsites	55
Total fixed investment	165
Working capital	18.88

Production Cost Summary

	Units/lb	Price ($/unit)	Annual Cost ($ 10^3)	$/lb
Raw Materials and By-Products				
Cyclohexane (lb)	0.740	0.43	63,672	
Nitric acid (lb)	0.821	0.18	29,556	
Catalyst & chemicals			3,400	
Net Raw Materials Cost			96,628	0.48
Utilities				
Power (kWh)	0.166	0.081	2,689	
Cooling water (10^3 gal)	0.074	0.12	1,776	
Process water (10^3gal)	0.001	1.35	270	
Fuel (10^6 Btu)	0	6.5	0	
Steam, 600 psi (10^3 lb)	0	9.5	0	
Steam, 150 psi (10^3 lb)	0	9	0	
Steam, 60 psi (10^3 lb)	0.011	8.9	19,580	
Inert gas (10^3 SCF)	0.0002	2	80	
Total Utilities Cost			24,395	0.12
Operating Costs				
Operators at $52,000 (6/shift)			1,435	
Foremen at $59,000 (2/shift)			543	
Supervision at $71,000/yr			71	
Maintenance material and labor (6% of TFI)			6,600	
Total Operating Costs			8,649	0.04
Overhead Expenses				
Direct overhead (45% labor + supervision)			922	
General plant overhead (65% operating costs)			5,621	
Insurance, taxes (1.5% of TFI)			2,475	
Total Overhead Expenses			9,018	0.05
TOTAL COST OF PRODUCTION			138,690	0.69
Depreciation (5 yr, straight line)			33,000	
TOTAL COST PLUS DEPRECIATION			171,690	0.86
SALES PRICE AT 15% DCF				1.12

Table A-11. Estimated Cost of Production of Maleic Anhydride via Butane

Basis: U.S. Gulf Coast in 1995
Capacity: 60 million lb/yr
Operating: 8,000 h/yr

Capital Cost Summary ($ 10^6)

Battery limits	105
Offsites	50
Total fixed investment	155
Working capital	7.62

Production Cost Summary

	Units/lb	Price ($/unit)	Annual Cost ($ 10^3)	$/lb
Raw Materials and By-Products				
n-butane (lb)	1.264	0.29	21,994	
Catalyst & chemicals			3,500	
Net Raw Materials Cost			25,494	0.42
Utilities				
Power (kWh)	0.7465	0.081	3,628	
Cooling water (10^3 gal)	0.042	0.12	199	
Process water (10^3gal)	0.00084	1.35	68	
Fuel (10^6 Btu)	0	6.5	0	
Steam, 600 psi (10^3 lb)	-0.0065	9.5	-3,705	
Steam, 150 psi (10^3 lb)	0	9	0	
Steam, 60 psi (10^3 lb)	0	8.9	0	
Inert gas (10^3 SCF)	0.0002	2	0	
Total Utilities Cost			293	0.00
Operating Costs				
Operators at $52,000 (2/shift)			478	
Foremen at $59,000 (0.5/shift)			136	
Supervision at $71,000/yr			0	
Maintenance material and labor (6% of TFI)			6,300	
Total Operating Costs			6,914	0.12
Overhead Expenses				
Direct overhead (45% labor + supervision)			276	
General plant overhead (65% operating costs)			4,494	
Insurance, taxes (1.5% of TFI)			2,325	
Total Overhead Expenses			7,096	0.12
TOTAL COST OF PRODUCTION			39,797	0.66
Depreciation (5 yr, straight line)			31,000	
TOTAL COST PLUS DEPRECIATION			70,797	1.18
SALES PRICE AT 15% DCF				1.74

Table A-12. Estimated Cost of Production of n-Butanol via Furan

Basis: U.S. Gulf Coast in 1995
Capacity: 200 million lb/yr
Operating: 8,000 h/yr

Capital Cost Summary ($ 10^6)

Battery limits	90
Offsites	45
Total fixed investment	135
Working capital	15.30

Production Cost Summary

	Units/lb	Price ($/unit)	Annual Cost ($ 10^3)	$/lb
Raw Materials and By-Products				
Furan (lb)	1.55	0.25	77,500	
Hydrogen, (10^3 SCF)	0.015	12	36,000	
THF (lb)	-0.33	0.85	-56,100	
Catalyst & chemicals			2,500	
Net Raw Materials Cost			59,900	0.30
Utilities				
Power (kWh)	0.75	0.081	12,150	
Cooling water (10^3 gal)	0.01	0.12	240	
Process water (10^3gal)	0	1.35	0	
Fuel (10^6 Btu)	0.1	6.5	13,000	
Steam, 600 psi (10^3 lb)	0.005	9.5	9,500	
Steam, 150 psi (10^3 lb)	0	9	0	
Steam, 60 psi (10^3 lb)	0	8.9	0	
Inert gas (10^3 SCF)	0.0002	2	80	
Total Utilities Cost			34,970	0.17
Operating Costs				
Operators at $52,000 (4/shift)			957	
Foremen at $59,000 (1/shift)			271	
Supervision at $71,000/yr			0	
Maintenance material and labor (6% of TFI)			5,400	
Total Operating Costs			6,628	0.03
Overhead Expenses				
Direct overhead (45% labor + supervision)			553	
General plant overhead (65% operating costs)			4,308	
Insurance, taxes (1.5% of TFI)			2,025	
Total Overhead Expenses			6,886	0.03
TOTAL COST OF PRODUCTION			108,384	0.54
Depreciation (5 yr, straight line)			27,000	
TOTAL COST PLUS DEPRECIATION			135,384	0.68
SALES PRICE AT 15% DCF				0.88

Table A-13a. Estimated Cost of Production of 1,3-Butadiene via THF

Basis: U.S. Gulf Coast in 1995
Capacity: 500 million lb/yr
Operating: 8,000 h/yr

Capital Cost Summary (\$ 10^6)

Battery limits	180
Offsites	90
Total fixed investment	270
Working capital	94.06

Production Cost Summary

	Units/lb	Price (\$/unit)	Annual Cost (\$ 10^3)	\$/lb
Raw Materials and By-Products				
THF (lb)	1.4	0.85	595,000	
Catalyst & chemicals			8,800	
Net Raw Materials Cost			603,800	1.21
Utilities				
Power (kWh)	1	0.081	40,500	
Cooling water (10^3 gal)	0.05	0.12	3,000	
Process water (10^3gal)	0.001	1.35	675	
Fuel (10^6 Btu)	-0.001	6.5	3,250	
Steam, 600 psi (10^3 lb)	0.005	9.5	23,750	
Steam, 150 psi (10^3 lb)	-0.0065	9	-29,250	
Steam, 60 psi (10^3 lb)	0	8.9	0	
Inert gas (10^3 SCF)	0.001	2	1,000	
Total Utilities Cost			42,925	0.09
Operating Costs				
Operators at \$52,000 (5/shift)			1,196	
Foremen at \$59,000 (1/shift)			271	
Supervision at \$71,000/yr			71,000	
Maintenance material and labor (6% of TFI)			10,800	
Total Operating Costs			83,267	0.17
Overhead Expenses				
Direct overhead (45% labor + supervision)			32,610	
General plant overhead (65% operating costs)			54,124	
Insurance, taxes (1.5% of TFI)			4,050	
Total Overhead Expenses			90,784	0.18
TOTAL COST OF PRODUCTION			820,777	1.64
Depreciation (5 yr, straight line)			54,000	
TOTAL COST PLUS DEPRECIATION			874,777	1.75
SALES PRICE AT 15% DCF				2.12

Table A-13b. Estimated Cost of Production of 1,3-Butadiene via THF

Basis: U.S. Gulf Coast in 1995
Capacity: 500 million lb/yr
Operating: 8,000 h/yr

Capital Cost Summary ($ 10^6)

Battery limits	180
Offsites	90
Total fixed investment	270
Working capital	57.04

Production Cost Summary

	Units/lb	Price ($/unit)	Annual Cost ($ 10^3)	$/lb
Raw Materials and By-Products				
THF (lb)	1.4	0.30	210,000	
Catalyst & chemicals			8,800	
Net Raw Materials Cost			218,800	0.44
Utilities				
Power (kWh)	1	0.081	40,500	
Cooling water (10^3 gal)	0.05	0.12	3,000	
Process water (10^3gal)	0.001	1.35	675	
Fuel (10^6 Btu)	0.001	6.5	3,250	
Steam, 600 psi (10^3 lb)	0.005	9.5	23,750	
Steam, 150 psi (10^3 lb)	-0.0065	9	-29,250	
Steam, 60 psi (10^3 lb)	0	8.9	0	
Inert gas (10^3 SCF)	0.001	2	1,000	
Total Utilities Cost			42,925	0.09
Operating Costs				
Operators at $52,000 (5/shift)			1,196	
Foremen at $59,000 (1/shift)			271	
Supervision at $71,000/yr			71,000	
Maintenance material and labor (6% of TFI)			10,800	
Total Operating Costs			83,267	0.17
Overhead Expenses				
Direct overhead (45% labor + supervision)			32,610	
General plant overhead (65% operating costs)			54,124	
Insurance, taxes (1.5% of TFI)			4,050	
Total Overhead Expenses			90,784	0.18
TOTAL COST OF PRODUCTION			435,777	0.87
Depreciation (5 yr, straight line)			54,000	
TOTAL COST PLUS DEPRECIATION			489,777	0.98
SALES PRICE AT 15% DCF				1.24

Table A-13c. Estimated Cost of Production of 1,3-Butadiene via THF

Basis: U.S. Gulf Coast in 1995
Capacity: 500 million lb/yr
Operating: 8,000 h/yr

Capital Cost Summary ($ 10^6)

Battery limits	180
Offsites	90
Total fixed investment	270
Working capital	36.85

Production Cost Summary

	Units/lb	Price ($/unit)	Annual Cost ($ 10^3)	$/lb
Raw Materials and By-Products				
THF (lb)	1.4	0	0	
Catalyst & chemicals			8,800	
Net Raw Materials Cost			8,800	0.02
Utilities				
Power (kWh)	1	0.081	40,500	
Cooling water (10^3 gal)	0.05	0.12	3,000	
Process water (10^3gal)	0.001	1.35	675	
Fuel (10^6 Btu)	0.001	6.5	3,250	
Steam, 600 psi (10^3 lb)	0.005	9.5	23,750	
Steam, 150 psi (10^3 lb)	-0.0065	9	-29,250	
Steam, 60 psi (10^3 lb)	0	8.9	0	
Inert gas (10^3 SCF)	0.001	2	1,000	
Total Utilities Cost			42,925	0.09
Operating Costs				
Operators at $52,000 (5/shift)			1,196	
Foremen at $59,000 (1/shift)			271	
Supervision at $71,000/yr			71,000	
Maintenance material and labor (6% of TFI)			10,800	
Total Operating Costs			83,267	0.17
Overhead Expenses				
Direct overhead (45% labor + supervision)			32,610	
General plant overhead (65% operating costs)			54,124	
Insurance, taxes (1.5% of TFI)			4,050	
Total Overhead Expenses			90,784	0.18
TOTAL COST OF PRODUCTION			225,777	0.45
Depreciation (5 yr, straight line)			54,000	
TOTAL COST PLUS DEPRECIATION			279,777	0.56
SALES PRICE AT 15% DCF				0.76

Table A-14. Estimated Cost of Production of Styrene via Butadiene

Basis: U.S. Gulf Coast in 1995
Capacity: 10^9 lb/yr
Operating: 8,000 h/yr

Capital Cost Summary ($ 10^6)

Battery limits	240
Offsites	75
Total fixed investment	315
Working capital	123.37

Production Cost Summary

	Units/lb	Price ($/unit)	Annual Cost ($ 10^3)	$/lb
Raw Materials and By-Products				
Butadiene (lb)	1.287	0.76	978,120	
Toluene (lb)	-0.0293	0.33	-9,669	
Benzene (lb)	-0.0103	0.44	-4,532	
Condensate (lb)	-0.0025	0.85	-2,125	
Catalyst & chemicals			8,800	
Net Raw Materials Cost			970,594	0.97
Utilities				
Power (kWh)	0.0886	0.081	7,177	
Cooling water (10^3 gal)	0.025	0.12	3,000	
Process water (10^3gal)	0	1.35	0	
Fuel (10^6 Btu)	0.0027	6.5	17,550	
Steam, 600 psi (10^3 lb)	0.0071	9.5	67,450	
Steam, 150 psi (10^3 lb)	0	9	0	
Steam, 60 psi (10^3 lb)	0	8.9	0	
Inert gas (10^3 SCF)	0	2	0	
Total Utilities Cost			95,177	0.10
Operating Costs				
Operators at $52,000 (5/shift)			1,196	
Foremen at $59,000 (1/shift)			271	
Supervision at $71,000/yr			71	
Maintenance material and labor (6% of TFI)			14,400	
Total Operating Costs			15,938	0.02
Overhead Expenses				
Direct overhead (45% labor + supervision)			692	
General plant overhead (65% operating costs)			10,360	
Insurance, taxes (1.5% of TFI)			4,725	
Total Overhead Expenses			15,777	0.02
TOTAL COST OF PRODUCTION			1,097,466	1.10
Depreciation (5 yr, straight line)			63,000	
TOTAL COST PLUS DEPRECIATION			1,160,486	1.16
SALES PRICE AT 15% DCF				1.37

Table A-15. Estimated Cost of Production of Adipic Acid via THF

Basis: U.S. Gulf Coast in 1995
Capacity: 200 million lb/yr
Operating: 8,000 h/yr

Capital Cost Summary ($ 10^6)

Battery limits	75
Offsites	55
Total fixed investment	130
Working capital	18.36

Production Cost Summary

	Units/lb	Price ($/unit)	Annual Cost ($ 10^3)	$/lb
Raw Materials and By-Products				
THF (lb)	0.62	0.85	105,400	
CO (10^3 SCF)	0.0062	6	7,440	
Catalyst & chemicals			4,000	
Net Raw Materials Cost			116,840	0.58
Utilities				
Power (kWh)	0.1	0.081	1,620	
Cooling water (10^3 gal)	0.07	0.12	1,680	
Process water (10^3gal)	0.0012	1.35	324	
Fuel (10^6 Btu)	0	6.5	0	
Steam, 600 psi (10^3 lb)	0	9.5	0	
Steam, 150 psi (10^3 lb)	0	9	0	
Steam, 60 psi (10^3 lb)	0.01	8.9	17,800	
Inert gas (10^3 SCF)	0.0002	2	8	
Total Utilities Cost			21,432	0.11
Operating Costs				
Operators at $52,000 (6/shift)			1,435	
Foremen at $59,000 (1/shift)			271	
Supervision at $71,000/yr			71	
Maintenance material and labor (6% of TFI)			4,500	
Total Operating Costs			6,278	0.03
Overhead Expenses				
Direct overhead (45% labor + supervision)			800	
General plant overhead (65% operating costs)			4,080	
Insurance, taxes (1.5% of TFI)			1,950	
Total Overhead Expenses			6,830	0.03
TOTAL COST OF PRODUCTION			151,380	0.76
Depreciation (5 yr, straight line)			26,000	
TOTAL COST PLUS DEPRECIATION			177,380	0.89
SALES PRICE AT 15% DCF				1.11

Table A-16a. Estimated Cost of Production of Maleic Anhydride via Furan

Basis: U.S. Gulf Coast in 1995
Capacity: 60 million lb/yr
Operating: 8,000 h/yr

Capital Cost Summary ($ 10^6)

Battery limits	105
Offsites	50
Total fixed investment	155
Working capital	7.12

Production Cost Summary

	Units/lb	Price ($/unit)	Annual Cost ($ 10^3)	$/lb
Raw Materials and By-Products				
Furan (lb)	1.1	0.25	16,500	
Catalyst & chemicals			3,500	
Net Raw Materials Cost			20,000	0.33
Utilities				
Power (kWh)	0.75	0.081	3,645	
Cooling water (10^3 gal)	0.042	0.12	302	
Process water (10^3gal)	0.00084	1.35	68	
Fuel (10^6 Btu)	0	6.5	0	
Steam, 600 psi (10^3 lb)	0	9.5	0	
Steam, 150 psi (10^3 lb)	-0.0065	9	-3,510	
Steam, 60 psi (10^3 lb)	0	8.9	0	
Inert gas (10^3 SCF)	0	2	0	
Total Utilities Cost			505	0.01
Operating Costs				
Operators at $52,000 (2/shift)			478	
Foremen at $59,000 (0.5/shift)			136	
Supervision at $71,000/yr			0	
Maintenance material and labor (6% of TFI)			6,300	
Total Operating Costs			6,914	0.12
Overhead Expenses				
Direct overhead (45% labor + supervision)			276	
General plant overhead (65% operating costs)			4,494	
Insurance, taxes (1.5% of TFI)			2,325	
Total Overhead Expenses			7,096	0.12
TOTAL COST OF PRODUCTION			34,515	0.58
Depreciation (5 yr, straight line)			31,000	
TOTAL COST PLUS DEPRECIATION			65,515	1.09
SALES PRICE AT 15% DCF				1.64

Table A-16b. Estimated Cost of Production of Maleic Anhydride via Furan

Basis: U.S. Gulf Coast in 1995
Capacity: 60 million lb/yr
Operating: 8,000 h/yr

Capital Cost Summary ($ 10^6)

Battery limits	105
Offsites	50
Total fixed investment	155
Working capital	7.44

Production Cost Summary

	Units/lb	Price ($/unit)	Annual Cost ($ 10^3)	$/lb
Raw Materials and By-Products				
Furan (lb)	1.1	0.30	19,800	
Catalyst & chemicals			3,500	
Net Raw Materials Cost			23,300	0.39
Utilities				
Power (kWh)	0.75	0.081	3,645	
Cooling water (10^3 gal)	0.042	0.12	302	
Process water (10^3gal)	0.00084	1.35	68	
Fuel (10^6 Btu)	0	6.5	0	
Steam, 600 psi (10^3 lb)	0	9.5	0	
Steam, 150 psi (10^3 lb)	-0.0065	9	-3,510	
Steam, 60 psi (10^3 lb)	0	8.9	0	
Inert gas (10^3 SCF)	0	2	0	
Total Utilities Cost			505	0.01
Operating Costs				
Operators at $52,000 (2/shift)			478	
Foremen at $59,000 (0.5/shift)			136	
Supervision at $71,000/yr			0	
Maintenance material and labor (6% of TFI)			6,300	
Total Operating Costs			6,914	0.12
Overhead Expenses				
Direct overhead (45% labor + supervision)			276	
General plant overhead (65% operating costs)			4,494	
Insurance, taxes (1.5% of TFI)			2,325	
Total Overhead Expenses			7,096	0.12
TOTAL COST OF PRODUCTION			37,815	0.63
Depreciation (5 yr, straight line)			31,000	
TOTAL COST PLUS DEPRECIATION			68,815	1.15
SALES PRICE AT 15% DCF				1.71

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