Technical and Economic Analysis of Lignin Conversion to Methyl Aryl Ethers

PAUL W. BERGERON* AND NORMAN D. HINMAN

Engineering Research Section, Biotechnology Research Branch, Solar Fuels Research Division, Solar Energy Research Institute, 1617 Cole Boulevard, Golden, CO 80401

ABSTRACT

The economical use of lignocellulosics for the production of liquid fuel depends on the efficient utilization of all the components in the feed material. Lignin can be converted to methyl aryl ethers (MAE's), products with blending octane numbers and Reid vapor pressures that make them excellent candidates for use as octane enhancers in gasoline.

An engineering design and economic analysis has been completed that investigated several production scenarios for the conversion of lignin to methyl aryl ethers. It was found that at oil prices of approximately $25/barrel and with improvements in product yields from the lignin hydrocracker and MAE synthesis reactors and with the recovery and recycle of the excess hydrogen in the product stream leaving the hydrocracker, it would be more economical to convert the lignin produced in a wood-to-ethanol plant to MAE's than to use it as boiler fuel for the ethanol plant.

Index Entries: Lignin; methyl aryl ethers; hydrocracking; economics; processes.

INTRODUCTION

The economical use of lignocellulosics for the production of liquid fuel depends on the efficient utilization of all the components in the feed material. Economic studies to date of the wood-to-ethanol process have assumed that the lignin fraction of woody biomass is burned for process fuel requirements. Alternatively, the lignin itself can be converted to a

*Author to whom all correspondence and reprint requests should be addressed.

salable fuel product. Since lignin is a long-chain, phenolic-based mole-
cule, it can be converted to a mixture of aromatic compounds that can be
further reacted with methanol and a suitable catalyst to produce methyl
aryl ethers (MAE's). Mixtures of MAE's have been found to have blend-
ing octane numbers and Reid vapor pressures that make them excellent
candidates for use as octane enhancers in gasoline. These characteristics
and their high volumetric heating value make them comparable to toluene
as a blending agent.

PROCESS DESCRIPTION

Feedstock and Manufacturing Cost Basis

In the MAE plant design, it was assumed that the lignin would be pro-
duced in a 51.5 MM gal/year ethanol plant that used an aspen wood
feedstock with a 24% lignin content. MAE production varied between ap-
proximately 20 and 30 MM gal/year depending on the design assumptions
of each case studied. The lignin and ethanol facilities were treated as sep-
arate entities that would exchange energy and material at cost. The ethanol
plant conversion process included dilute acid prehydrolysis, enzymatic
hydrolysis, and fermentation of both five-carbon and six-carbon sugars.
Previously, in the design and economics of such ethanol facilities, it was
assumed that the lignin would be burned for process heat, and in doing
so, the energy requirements of the plant were met. Therefore, the cost of
the lignin to the MAE facility was set at the cost incurred by the ethanol
facility to buy the additional wood chips necessary to replace the lost fuel
value of the lignin. The lignin cost was calculated to be 2.56 cents/lb lignin.

The lignin was normally sent to the utilities section of the ethanol
facility with a moisture content of 55% (wet basis) and then dried to 41%
moisture prior to burning. It was decided to send the 55% moist lignin to
the MAE facility, that would then incur the cost of drying from that
level. This was done because the amount and moisture content (50%) of
the "green" replacement wood for fuel required removal of the same
amount of water to get to the 41% moisture level. This involved no design
changes to the ethanol facility and had no impact on the economics of
ethanol production.

The only other exchange between the ethanol and lignin facilities was
the shipping from the lignin to the ethanol facility of process gas and
heavy liquids generated in the lignin hydrocracker and not required as
fuel in the lignin facility. The lignin facility was credited at the rate of
$2.44/MMBTU, the fuel value of wood. Steam was assumed to be gener-
ated on site at a cost of $5.50/MMBTU. Electricity was purchased at a cost
of 2.92 cents/kilowatt hour. These costs are consistent with those pre-
viously used for the analysis of the ethanol facility. In addition to these
operating costs, the lignin facility must import natural gas to produce

hydrogen and methanol to convert, to ethers, the phenols produced in the hydrocracker. Since the prices for these feedstocks fluctuate a great deal owing to market forces, they were treated as described below in the section on economic analysis.

Economic Assumptions

The assumptions used to calculate the annual cost of the various scenarios were based on the uniform cost estimation method developed at Argonne National Laboratory (1) and include: financing at 70% equity at a 15% rate of return and 30% debt at an interest rate of 11%, 20 yr project life, a labor rate of $15.40/h with man hours of labor per year calculated as 0.1% of the total investment, maintenance cost at 4% of total investment, overhead at 60% of the labor plus maintenance cost total, and 1988 equipment purchasing costs.

Design Basis

The MAE facility is divided into six sections. In the "Lignin Storage and Preparation Section," the lignin is received, stored, and dried. The design of this section is unaffected by the various changes is downstream design and performance included in the design cases of this study. The flow rates are the same for cases 1–5. In case 6, the incoming lignin is assumed to be dry. The capital and operating costs for all of the cases are dominated by the flash drying system, which removes 95% of the approximately 48,000 lb/h of water entering with the lignin. The remaining 5% of the moisture is assumed to be removed in the dry lignin storage bins, which are continually swept with carbon dioxide to remove free oxygen from the lignin prior to its introduction into the hydrocracker. The drying system design and cost are based on a Flakt flash drying system incorporated in the ethanol facility design previously done by Badger Engineers (2). The drying system accounts for all of the fuel requirements, essentially all of the electrical requirements, and 88% of the capital charges of this section. The remainder of this section comprises standard solids handling and storage equipment.

Natural gas is imported to the "Steam Reforming Section" to produce hydrogen for the lignin hydrocracker. Since this is a standard industrial operation, the design and economics for this section were taken from Volume 5 of the Chemical Processing and Engineering series (3). The size and flow rates of the steam reforming section are dictated by the incorporation or not of hydrogen recycling into the design of the case under consideration.

The "Hydrocracker Section" (Fig. 1) includes a mixer to blend the lignin with the carrier fluid, a process gas-fired preheater, to raise the temperature of the lignin-carrier fluid-hydrogen feed stream to 454°C, the hydrocracker itself, and a catalyst removal/addition system. The carrier fluid is a partially-reacted lignin pasting oil that is recycled from the
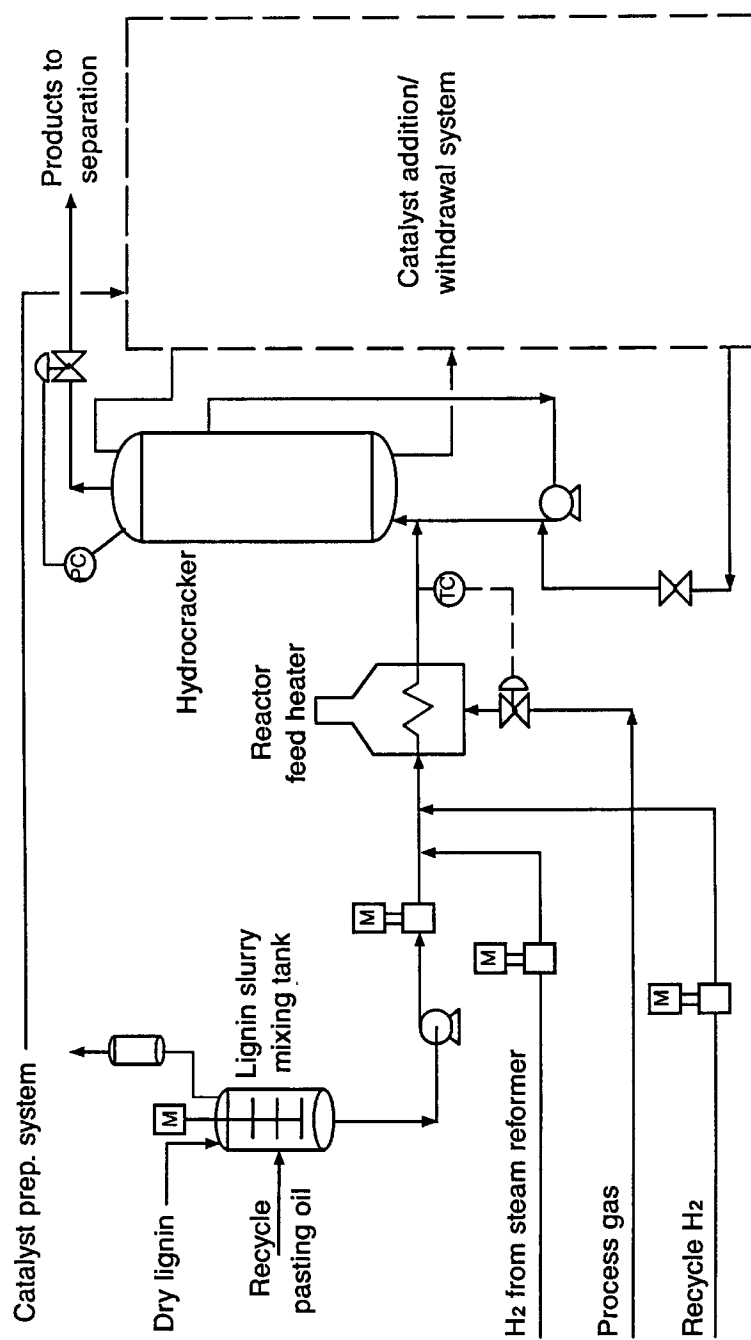
Fig. 1. "Hydrocracker Section" in which the dried lignin is cracked from its polymeric state.

product separation section downstream of the hydrocracker. The design of the hydrocracker is based on the reactor conditions and the resulting product yields obtained by the Hydrocarbon Research Institute (HRI) in their experimental work on lignin hydrotreating in the 1960s and early 1980s (4–6). An iron on alumina catalyst was used in the earlier work, whereas the later work involved the use of an unspecified, but probably cobalt–molybdenum based, catalyst. The mass balance around the hydrocracker was based on the HRI publications in the 1980s which, however, did not list the exact composition of the C1–C5 fraction of the products. This composition was assumed to be the same as published in the 1972 patent for lack of any better information. The hydrocracking reactor conditions (441°C, 6900kPa, 0.238 kg of hydrogen/kg of dry lignin, 375 kg of dry lignin/h/m³ of reactor, 3 kg of pasting oil/kg of dry lignin) were taken from the 1972 patent.

The bone-dry lignin is introduced through a star valve into the slurry preparation tank, which is operated at near-ambient pressure to avoid the plugging of and leakage through the feeder. The hydrogen is compressed from 1725 kPa at the steam reforming section exit to 7600 kPa and added to the lignin-pasting oil slurry, which has also been pumped up to 7600 kPa. This mixture is heated to 454°C in a process-gas fired heater prior to being fed to the hydrocracker. The hydrocracker is operated as a three-phase ebullated bed, as has been done in coal liquefaction pilot plants in the 1970s and 1980s. The liquid phase containing the solid catalyst is pumped from the top of the reactor to the feed point at the bottom of the reactor to obtain the appropriate liquid residence time. The gaseous product stream disengages from the liquid at the top of the reactor and is sent to the "Phenols Separation Section." The catalyst is replenished intermittently through purging approximately 3200 kg of reactor liquid once a week and adding approximately 68 kg of fresh catalyst. The design for this section was the same for all of the cases. It was assumed that the increase in hydrocracker yield in cases 5 and 6 could be achieved with the same hydrocracker design through the use of an improved catalyst. The lignin, hydrogen, and pasting oil flow rates are the same for all six cases. The product flow rates are the same for cases 1–4, but were adjusted to reflect the mass balance assumed for the increased yield from the hydrocracker in cases 5 and 6.

The product stream of the hydrocracker is separated into three streams in the "Phenols Recovery Section" (Fig. 2): (1) a permanent gas stream for recovery of excess hydrogen for recycle and/or process gas for energy production; (2) a liquid stream containing the aromatic compounds to be sent to the MAE synthesis reactor; and (3) a heavy liquid stream composed of incompletely reacted dimer and trimer lignin fragments to be recycled as pasting oil to the slurry preparation tank. A relatively small stream is bled from the heavy liquid stream to remove the ash introduced with the lignin. This bleed stream is used to provide additional process heat.
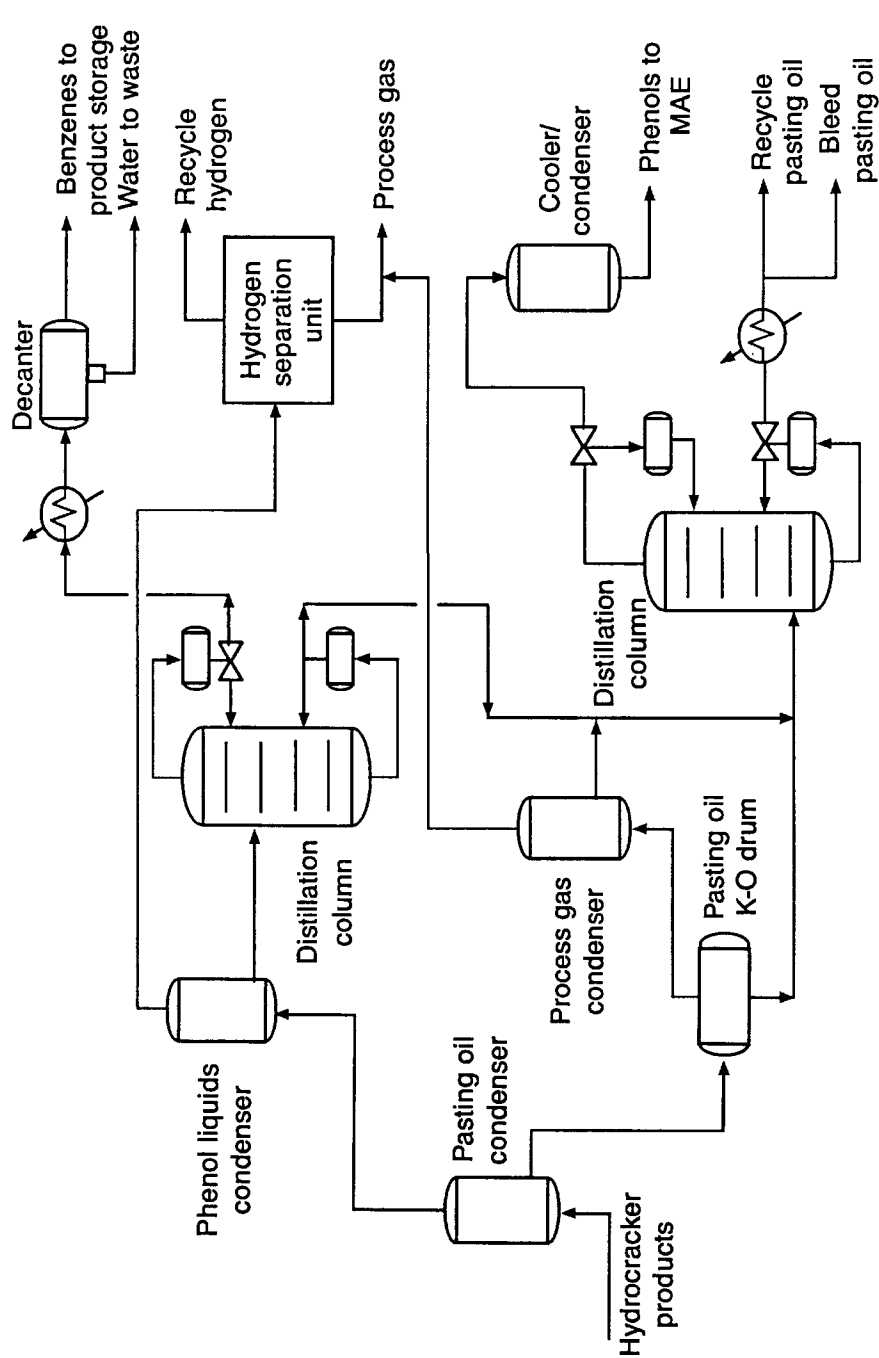
Fig. 2. "Phenols Recovery Section" in which the hydrocracker product is separated into gaseous, product, and recycle streams.

The separations in this section were designed with the aid of the ASPEN/SP simulator. The pasting oil was assumed to be 1-methylnaphthalene (a pasting oil in coal liquefaction processes), the mixture of phenols was assumed to be exclusively phenol, and the neutral fraction was assumed to be toluene. This was done because these compounds were in the data bank of the simulator and the actual compounds were not.

The process gas stream was separated from the liquid product at the hydrocracker exit pressure (6900 kPa) and sent through a membrane separation system to remove the hydrogen for those cases incorporating hydrogen recycle. With this system, it was possible to recycle a 99% pure hydrogen stream containing 91.5% of the excess hydrogen leaving the hydrocracker, according to information obtained from a leading manufacturer.

The "Ether Synthesis Section" (Fig. 3) contains the ether synthesis reactor and downstream product separation equipment. Methyl phenyl ether (MPE) is currently manufactured via the Williamson Synthesis by a two-step reaction in which phenol is reacted with sodium hydroxide, and the product converted to MPE by reaction with either methyl chloride or dimethylsulfate. Since the cost of the reactants is prohibitively high, a catalytic approach that combines phenol and methanol was chosen for this study. Some, but not much, work has been done on this approach, which is outlined in the section that follows on sensitivity analysis. The separations in this section were also done with the aid of the ASPEN/SP simulator. The ethers were assumed to be methyl-phenyl ketone, and the mixture of phenols was assumed to be phenol since these compounds were available in the simulator's data bank.

SENSITIVITY ANALYSIS

The sensitivity of MAE product cost to changes in four process parameters was examined. The four parameters are: hydrocracker reactor yield, phenol conversion per pass in the ether reactor, hydrogen recovery and recycle, and lignin moisture content. Six cases were investigated to determine the sensitivity of the economics to these four parameters. The results and the assumptions for each case are presented in Table 1. The methanol and natural gas costs are based on their prices at the time of the study. These costs can be adjusted with the factors listed in Table 2 to reflect the prices used in the case studies for the $15 and $35/barrel oil price scenarios (see, next section on pricing strategy). In addition to these parameters, the economic effect of changing the size of the lignin feed stream and, therefore, the lignin conversion plant was estimated. All of these comparisons were made using the MAE selling prices based on the $15/barrel of oil scenario. The results of this exercise are presented in Table 3.
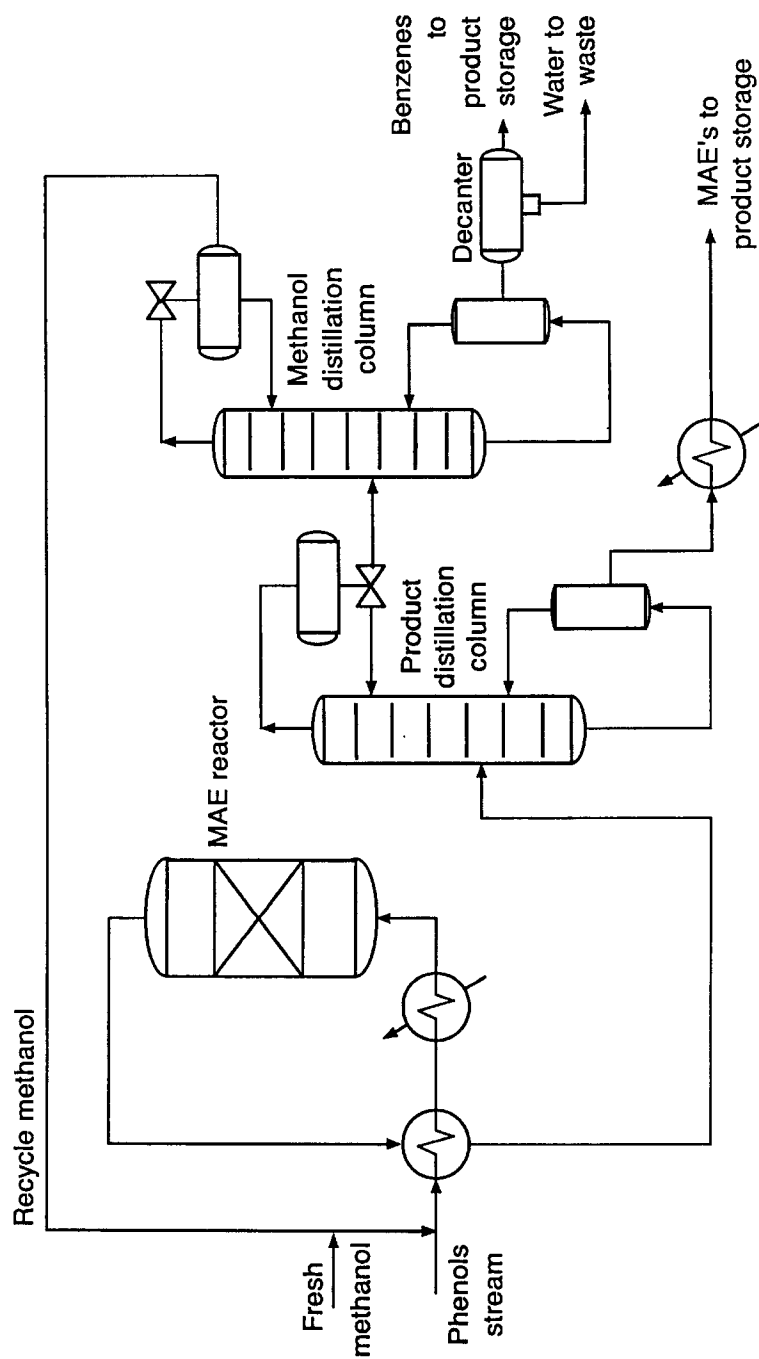
Fig. 3. "Ether Synthesis Section" in which the hydrocracker product is converted into the final ether mixture.

Table 1
Results from the Six Cases Studied:
The Change in Ethanol Selling Price Based on the MAE Price Relative to Price of Toluene/Xylene Mixture

Case	Oil price, $/bbl	Hydrogen recycle	Hydrocracker yield, %	Phenols conversion	Lignin water content, %	Reactant cost, cents/gal MAE	MAE price, cents/gal	Ethanol cost change, cents/gal
1	15	N	48	23	55	97	152	+34
	35					148	203	+23
2	15	N	48	100	55	94	134	+30
	35					144	184	+14
3	15	Y	48	23	55	79	131	+29
	35					104	157	+ 3
4	15	Y	48	100	55	81	119	+21
	35					103	141	− 4
5	15	Y	72	100	55	57	93	+17
	35					74	111	−24
6	15	Y	72	100	0	40	76	+ 7
	35					59	95	−32

Table 2
Prices of Chemicals Relevant to the Study for Two Oil Price Scenarios

	Ratio to Oil in $/bbl	Cost at $15/bbl oil	Cost at $35/bbl oil
MTBE, cents/gal	3.9	59	137
Toluene/xylenes, cents/gal	4.3	65	151
Methanol, cents/gal	2.3	35	81
Natural gas, $/1000 ft^3	0.141	2.12	4.94

Table 3
Economic Effect of Varying Lignin Flowrate

Case	Relative lignin flowrate	Breakeven Oil Price, $/bbl		
		Case 4	Case 5	Average
A	1	32	23	28
B	2	28	21	25
C	3	26	20	23
D	2/3	35	25	30
E	1/3	40	28	34

The hydrocracker yield parameter was varied from 48 to 72%. The 48% yield was achieved by researchers at the Hydrocarbon Research Institute in experiments conducted in 1980, which served as a basis for a patent issued in 1981 (3). The 72% yield is believed to approximate the theoretical limit for the conversion of lignin to phenols, which are the precursors of the MAE's. The figure is approximate because the exact structure of the lignin feedstock is uncertain at this time. The increased yield

was found to reduce the selling price of the MAE product by 22% (case 3 vs case 4 in Table 2).

The conversion of phenols in one pass through the ether synthesis reactor was set at 23 and 100%. The 23% conversion was achieved by Russian researchers and disclosed in a 1982 patent (7). The research was focused on improving the selectivity of the catalytic conversion of phenol to methyl aryl ether, thus excluding the variety of other products that may be formed in such reactions. They used no excess methanol and achieved a 97% selectivity, but only a 23% phenol conversion. No attempt was reported to recycle the product stream or increase the residence time in the reactor to improve the conversion. Since the effect of either was not known, the MAE synthesis section was configured to remove the unreacted phenol from the reactor effluent stream and return it to the reactor with the fresh feed. If this is done to simulate 12 passes through the reactor, then a 96% overall conversion is achieved. This was compared to a case with 100% ether yield achieved in one pass through the reactor and 50% excess methanol. It was found that a 12% reduction in product selling price could be achieved with this improvement in conversion per pass (case 1 vs case 2 in Table 2).

When recovery and recycle of hydrogen is incorporated into the process, the product selling price decreases by 14% (case 2 vs case 3 in Table 2). The recovery was done using a membrane separation system currently available on the market. When the hydrogen was not recycled, it was included in the process gas to produce energy for process requirements or for sale to the ethanol facility. The effect is large because the hydrocracking reactions have been found to require a large excess of hydrogen to proceed with adequate efficiency. The excess hydrogen leaving the reactor is an expensive fuel if not recycled.

When the lignin moisture content was ignored and the associated drying-related equipment and operating costs were removed from the flowsheet, the product cost fell by 18% (case 5 vs case 6 in Table 2). This presumes that dry lignin could be purchased at the same price as that paid for the wet lignin, or that the drying equipment capital and operating costs can be reduced to insignificance. Although this is not practical for the particular process considered in this study, it may be approached if an organosol pretreatment is used in the ethanol plant rather than the dilute acid pretreatment. The drying equipment assumed to be used was a flash drying system, as is ordinarily used in industry for such purposes. The capital cost of presently commercial systems is quite high when such a large volume of water is removed. The energy costs related to the removal of the water represent one-fifth of the annual drying costs and will remain approximately the same regardless of the drying method involved. This accounts for about 4 of the 18% cost reduction. The remaining 14% covers the capitol and electrical power costs of the drying equipment.

The lignin plant size depends on the amount of lignin available to it. The lignin from a 51.5 MM gallons/yr ethanol plant that uses a feedstock

with 24% lignin has so far been assumed to be available. If the size of the ethanol plant or the lignin fraction of the feedstock to it is different, the size and economics of the lignin conversion facility will change. Also, if other ethanol plants are in the vicinity, they may serve as lignin sources to one centrally located lignin facility. It was assumed that the change in MAE production cost could be calculated by changing the feedstock and utilities costs in direct proportion to the change in lignin feed rate and changing the capitol costs in proportion to the lignin feed rate ratio raised to the 0.6 power.

The impact on the break-even oil price of doubling, tripling, reducing by two-thirds, and reducing by one-third the lignin flow rate is presented in Table 3. The doubling or tripling of the lignin flow rate could result from either increasing the size of the adjacent ethanol facility or receiving the lignin from one or two nearby wood-to-ethanol plants. The reduction of the lignin flow rate could result from a smaller ethanol facility or a reduced lignin content in the feedstock to a 51.5 MM gal/yr ethanol facility. The assumption underlying the presentation of cases 4 and 5 is that research is capable of improving process performance to somewhere between case 4 (48% hydrocracker yield and 100% per pass conversion in the MAE synthesis reactor) and case 5 (72 and 100%, respectively). A reduction in drying costs would reduce the required reactor performance improvements necessary to achieve economic viability. As seen in Table 3, only for the lowest flow rate does the break-even oil price rise above the $35/barrel oil price scenario. The changes in break-even oil price are not more dramatic because the capitol charges are not a large fraction of the MAE production costs.

ECONOMIC ANALYSIS

Pricing Strategy

The prices of natural gas and the various commodity chemicals relevant to this study are important to the conclusions that can be drawn. These prices have fluctuated over the last 10 years, but trends can be observed when they are compared to the price of oil during that time. The ratios of the average prices for each year of these chemicals to the average price of oil for that year have been averaged for the past 10 years and are presented in Table 2. These averaged ratios have been used to calculate the probable prices for the natural gas and chemicals when the price of oil is $15 and $35/barrel. The chemical and natural gas prices corresponding to these two oil prices are also presented in Table 2. Methanol and natural gas are included because they are the only feedstocks to the MAE plant other than lignin. Methyl-tert-butyl-ether (MTBE) and a mix of toluene and xylenes are included because they represent the competition to MAE's for the octane enhancer market.

The current price of oil at the end of 1988 is approximately $15/barrel. The current natural gas price of $2.10/1000 ft^3 is nearly the same as that calculated using the 10-year average ratio shown in Table 2. However, methanol is currently selling for 60 cents/gal, compared to the price of 35 cents/gal calculated using the 10-year average ratio for methanol. This illustrates the effect of a temporary demand/supply imbalance, as currently exists for methanol. If the currently inflated methanol price were used to calculate the cost to the process for methanol, then the process would be penalized unjustifiably. No adjustments were made to any production costs other than methanol and natural gas for the $35/barrel oil price scenario since the degree of change would have been difficult or impossible to ascertain.

The use of price ratio averages also allows rational cost projections into the future. Once the selling price for the MAE product has been calculated, a benchmark is needed to determine its marketability at that price. The prices of MTBE and toluene/xylene in the second half of 1988 have been around 90 and 78 cents/gal, respectively. These prices also are higher than those calculated using the 10-year average ratios (with oil approximately at the current price), probably because of a temporary imbalance in market forces. The selling prices of the MAE product for each plant design scenario will be compared to the selling prices of the competition calculated using the average ratio technique for oil at $15 and $35/barrel. This will maintain consistency with the feedstock pricing and eliminate any undue influence from current market irregularities on determining the future marketability of the MAE product.

Case Study Results

The contribution of the reactants—dry lignin, hydrogen, and methanol—to the selling price of the MAE product for each case is presented in Table 1. The cost for dry lignin include the 2.56 cents/lb lignin charged by the ethanol facility and the capital and operating costs incurred for drying it. The annual cost for purchasing the lignin is $8.0 MM, and for drying it is $5.0 MM. The costs for hydrogen include the cost for natural gas feedstock, the capital and operating costs to reform the natural gas, and the capital and operating costs to recover and recycle the excess hydrogen for those cases that do this. The cost charged for hydrogen is reduced by the energy credit obtained from any hydrogen present in the process gas stream. The methanol charge is just the cost to purchase it. The hydrogen and methanol charges vary from case to case depending on the inclusion of hydrogen recycle, the use of excess methanol, and the oil cost scenario used. These reactant costs are a very large fraction of the cost of producing the MAE product ranging from 72 to 89% of the product selling price.

A list of MAE product selling prices for each case at both oil cost assumptions is presented in Table 1. They can be compared to the selling prices of the competition given in Table 2 to determine which seem eco-

nomically viable. Also listed is the impact on ethanol selling price if the MAE product were sold at the price of its closest competitor (the toluene/xylene mixture) and the difference between production cost and selling price absorbed by the ethanol facility. None of the design cases compares favorably to the competition when oil sells for $15/barrel, but several do compare favorably when oil sells for $35/barrel. The current state of the art is best represented by case 3 in which the hydrocracking and MAE synthesis reactor performances are based on actual laboratory results. With oil at $35/barrel, the price of MAE is only 6 cents higher than the projected market price of $1.51/gal of toluene/xylenes. The impact of selling the MAE product at $1.51 would be to raise the price of ethanol by 3 cents. If the price of oil were $37/barrel, then the MAE selling price for case 3 would be equivalent to the toluene/xylenes selling prices. This represents the break-even oil price for this case when compared to the alternate use of lignin, which is to burn it for process heat in the ethanol plant.

Case 1 is simply case 3 adjusted to exclude hydrogen recovery and recycle. The MAE selling price increases over case 3 for the two oil price scenarios, thus demonstrating the economic benefit of recycling hydrogen. Since the technical capability exists at present to recover the hydrogen, case 1 need be discussed no further. Case 2 is the same as case 1 except that the phenols conversion par pass was changed from 23 to 100% in order to observe the economic impact of this change.

If, as in case 4, the conversion of phenols in the MAE synthesis reactor can be raised to 100% in one pass, the price of the MAE product drops below the projected price of toluene/xylenes by 10 cents/gal. This represents a reduction in the selling price of ethanol of 4 cents/gallon. The break-even oil price for case 4 is $32/barrel. In case 5, the additional process improvement of the hydrocracker yield at its assumed theoretical limit was incorporated. This dropped the price to $1.11/gal, 40 cents below the projected price of toluene/xylenes. This results in a reduction of the ethanol selling price of 24 cents and a break-even oil price of $23/barrel. Although it is unlikely that such high yields of product could be achieved in either reactor, the size of the margin between the MAE and the TX selling prices implies that yields below those assumed would be acceptable and may be achieved with sufficient research. Case 6 was included to show the limit of the additional cost savings that may be realized if a more economical lignin drying system were found or could be developed, or if drier lignin was imported to the facility. The assumptions for case 6 result in an MAE selling price of 95 cents/gal. This corresponds to a ethanol selling price reduction of 32 cents/gal or a break-even oil price of $18/barrel.

CONCLUSIONS

At oil prices higher than current prices and with improvements in product yields from the hydrocracker and MAE synthesis reactors and

the recovery and recycle of the excess hydrogen in the product stream leaving the hydrocracker, it would be more economical to convert the lignin produced in a wood-to-ethanol plant to MAE's than to use it as boiler fuel for the ethanol plant. For case 5, which includes ideal yields from both reactors and a lignin moisture content of 55%, the MAE product becomes competitive in the octane enhancer market when the price of oil reaches $23/barrel.

The largest potential reduction in MAE selling price may be obtained from research aimed at increasing the yield from the lignin hydrocracking reactor. When this yield is increased from 48%, as obtained in the laboratory, to 72%, which approximates the theoretical yield, the MAE selling price decreases by 22%. Therefore, this represents the research area with the highest potential payoff.

When the MAE synthesis reactor per pass yield is raised from 23%, as obtained in the laboratory, to 100%, the MAE selling price drops 12%. This most likely represents a higher payoff than may be attained through efforts to reduce the drying equipment cost which, if cut in half (an ambitious goal), would reduce the MAE selling price by 7%. This statement is based on the fact that commercial drying systems are presently available, whereas the catalysts available for each reactor are the product of only limited laboratory-scale research, and the potential for catalyst improvements through research are quite high.

The recovery and recycle of the hydrogen in the hydrocracker effluent stream can be done very efficiently with currently available membrane systems. These systems have become industrially accepted in the 1980s and continue to be researched and developed aggressively by companies like Monsanto and Air Products. The results of this will be cheaper and improved membrane systems in the future.

ACKNOWLEDGMENT

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