uop

DOE/PC/90042--T17

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March 28, 1996

Mr James Huemmrich
U. S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940, MS 921-143
Pittsburgh, PA 15236

SUBJECT: **OXYGENATED OCTANE ENHANCERS: SYNGAS TO ISOBUTYLENE**
Contract Number: DE-AC22-91PC90042

Dear Mr. Huemmrich:

Enclosed find copies of the final version of Technical Progress Report No 19. This report has been approved by Dr. Arun Bose. This report contains patentable material which was disclosed in an earlier patent disclosure. Therefore it is marked "patent hold" on the appropriate pages.

If you have any questions concerning this report, please contact me at (847) 391-2038.

Regards,

Terry L. Marker
Sr. Development Specialist

TLM/bls

Enclosures

cc: Document Control Center - U.S. DOE-PETC - MS 921-143
Dr Arun Bose -- DOE PETC - MS 922
Sarla Nanda -- DOE PETC - MS 58-M217
RC/PF: NVD-Syngas to Isobutylene (DOE)
JBaptist, PTBarger, BVVora, TLMarker

CONTRACT TITLE AND NUMBER:
Development of a Catalyst for Conversion of Syngas-Derived Materials to Isobutylene
DE-AC22-91PC90042

Date:
Quarterly Report No. 19
Reporting Period:
10/1/95-12/31/95

Contractor:
UOP
50 E. Algonquin Rd.
Des Plaines, IL 60017-5016

Author:
Ben C. Spehlmann

Contract Period: March 15, 1991 to March 16, 1996

QUARTERLY TECHNICAL REPORT

The goals of this project are to develop a catalyst and process for the conversion of syngas to isobutanol. After identification and optimization of key catalyst and process characteristics, the commercial potential of the process is to be evaluated by an economic analysis.

From independent process variable studies to investigate the conversion of a methanol/ethanol feed to isobutanol, the best performance to date has been achieved with the 2% Pt on Zn/Mn/Zr oxide catalyst. At 325°C, 300 psig, 7/1 MeOH/EtOH molar feed ratio and 1 hr^{-1} MeOH WHSV, 22.2% selectivity to isobutanol is obtained with 55.2 and 97.0% conversions of methanol and ethanol, respectively[1]. Results of this "best case" run are being used as a basis for the economic evaluation.

Unfortunately, studies performed to examine the conversion of methanol alone (in the absence of ethanol) to isobutanol on the Pt on Zn/Mn/Zr oxide catalyst showed little promise. Even using the ethanol co-feed, isobutanol yields were similarly poor in the presence of high H_2 partial pressures representative of a methanol synthesis recycle gas loop. Therefore, the commercial system has been modeled based on a stand-alone isobutanol synthesis plant using ethanol co-feed. In addition to the single-pass product slate obtained in the pilot plant, the assumption of equilibrium CO, H_2O, CO_2, and H_2 makes was used.

Using Hyprotech Hysim v2.5 process simulation software, and considering both gas and liquid recycle loops in the process flow diagram, the overall carbon conversion is 98% with 22% selectivity to isobutanol. The expected production of isobutanol is 92 MT/day from 500 MT/day of methanol and 172 MT/day of ethanol feed. An additional 13 MT/day of isobutryaldehyde intermediate is recovered in the liquid product and vent streams. This material will be considered to have the same value as isobutanol for economic purposes, since it is conceivable that buildup of the C_4 aldehyde in the liquid and gas recycle loops would lead to its eventual conversion to the desired product. The capital cost estimate for a 20300 BPSD combined feed commercial isobutanol synthesis plant was estimated to be 5.9 MM dollars based on an extensively-licensed UOP technology which is similar in design.

The relationship between vent and purge stream losses and the separator temperature downstream of the reactor has been investigated. Flash calculations show some benefit in separating the reaction product mixture above cooling water (95°F) temperatures since light reaction byproducts are vaporized and purged in the vent stream. This reduces the liquid recycle stream and liquid product fractionation requirements. Vent losses become prohibitive economically, however, for separator temperatures above 150°F, since feed and product losses approach 5%. The optimal separator temperature was found to be approximately 120°F. This information was used for the economic evaluation of the commercial process.

Because of the low selectivity (22%) of the methanol conversion catalyst to isobutanol, the process is uneconomical, even if the isobutanol is valued as a solvent ($903/MT) and not as isobutylene for MTBE production ($352/MT). If the intermediate isobutryaldehyde is considered the same as isobutanol (valid if the aldehyde in liquid recycle of the commercial plant is hydrogenated), 26% selectivity to isobutanol can be achieved. Still, a selectivity of greater than 40% is needed for a 20% internal rate of return on the capital investment. The expected 1998 U.S. isobutanol consumption for solvent and other applications is 54,500 MT. A selectivity of at least 80% would be required for 20% IRR if isobutanol value is based on its gasoline (MTBE precursor) use. This market (10.6 million MT 1997 U.S. estimate) is substantially broader than the solvent market, and therefore a more reasonable basis for the economic analysis.

In summary, based on the experimentally investigated conditions and performance data, this particular process for the conversion of lower alcohols to higher branched oxygenates cannot produce isobutanol at a price which would allow penetration into the gasoline market. Therefore, no competition to the current state-of-the-art TBA byproduct dehydration route to isobutylene is provided. UOP does not intend to continue pursuing this technology further.

EXPERIMENTAL

All experimental work to optimize the catalyst formulation and reaction conditions has been completed. Details of procedures used for this work can be found in Quarterly Report No. 18 for the reporting period 7/1/95-9/30/95.

RESULTS AND DISCUSSION

Summary of Process Variable Studies/Optimum Conditions Obtained Experimentally

With the 2% Pt on Zn/Mn/Zr oxide catalyst, the best performance was achieved experimentally in pilot plant run 325 using 325°C, 300 psig, 1 hr^{-1} WHSV, and 7/1 methanol/ethanol molar feed ratio. The methanol conversion and carbon selectivity to isobutanol were 55.2% and 22.2%, respectively, the highest obtained in any testing performed to satisfy tasks 3 and 4 of the program. In view of the superior results of this test, these performance data were used as a basis for the economic evaluation of a commercial higher alcohols process according to Task 5 of the program.

One process concept for the integration of a higher alcohols process with a conventional methanol synthesis plant was to place the process immediately after the methanol synthesis reactor using imported ethanol. The advantage of this configuration would be that any CO and CO_2 formed in the higher alcohol synthesis reactor could be easily recycled to the methanol synthesis reactor for conversion to additional methanol using the existing recycle loop. Unfortunately, examination of the catalyst performance under the conditions representing a commercial methanol synthesis recycle gas stream (70-80 mole% H_2, 1000-1500 psig), showed very low conversion for both methanol and ethanol with only small amount of isobutanol formed.

Modeling of a Commercial Isobutanol Synthesis Plant

From the process optimization experimental results, a stand-alone isobutanol production plant operating at the "best-case" conditions (300 psig, 320°C, 1 hr^{-1} WHSV) was the basis for economic evaluation. The single-pass methanol and ethanol conversions (55.2% and 97.0%), selectivity to isobutanol (22.2%) and product slate obtained in pilot plant work were used to model the commercial system with Hyprotech Hysim v2.50 process simulation software.

For process modeling, it was assumed that methanol alone contributed to the formation of all single-carbon species (CO, CO_2), all C_1-C_5 hydrocarbons, and the methyl groups of dimethyl ether, methyl formate, methyl acetate, methyl butyl ether, and methyl isobutyrate. Furthermore, one carbon of the side products isopropanol and isopentanol was considered to originate from methanol. The smaller amounts of ethanol (12.5 mol-% of the liquid feed) charged were assumed to participate in producing all 2- and 4-carbon groups in the same ratios as shown in the yield data generated from pilot plant run 325. The remaining carbon needed to generate the product slate (after conversion of 97% of the ethanol) was presumed to stem from the feed methanol. Generation of water and hydrogen was observed experimentally, and yields of these products were in accordance with 100% elemental O and H balances. The water gas shift reaction was also modeled and assumed to achieve equilibrium at reaction temperature. A comparison of actual measured and theoretical gas yields, as well as a summary of the conditions and reaction coefficients used in modeling, is provided in Table 1.

Basis for Capital Cost Estimate

A fresh feed rate of 672 MT/day (5300 BPSD) methanol and ethanol, supplied from a methanol synthesis plant (500 MT/day, 4000 BPSD) and purchased ethanol (172 MT/day, 1300 BPSD) was chosen for the commercial simulation. Because of the low selectivity to the desired isobutanol, the substantial liquid recycle of byproducts along with the unconverted feed gave a combined reactor feed rate of 20300 BPSD. The liquid recycle purge rate was chosen to prohibit >1% loss of carbon contained in the feed and product streams. The equipment requirements for such a plant were similar to those for an isomerization technology (Penex) which UOP currently licenses extensively. Therefore, a capital cost estimate (+/- 30%) was prepared for the process based this well-established technology, excluding the costs of the makeup feed driers, makeup gas compressor, and product gas scrubber (Appendix I). The estimated erected cost was 5.9 MM dollars.

Process Simulation Results

Hyprotech Hysim v2.50 process simulation software was used with the NRTL activity property package (recommended for non-ideal components) to model the system. In the process flow diagram, shown in Figure 1, methanol and the ethanol co-feed are mixed and combined with recycle gas (CO, CO_2, and H_2) and then recycle liquid before being heated to the reactor inlet temperature. Although three reactors are illustrated to model methanol conversion, ethanol conversion and the water gas shift reaction, only one reactor would be used commercially. The reaction product is cooled and phase-separated. A significant portion of the separator gas is vented to prevent >25 psia hydrogen partial pressure in the combined reactor feed, since this condition gave poorer selectivity experimentally.

The separator liquid, containing isobutanol, unconverted methanol and ethanol, as well as a number of byproducts, is charged to a distillation column. Excess of 99% of the isobutanol is recoverable in the bottoms product with negligible losses of methanol and ethanol. The byproduct isobutyraldehyde is recovered in the overhead product. The extent of buildup of this species in the liquid recycle loop is difficult to estimate from experimental data, since hydrogenation of this material to isobutanol might eventually occur, improving the alcohol yield. Nevertheless, a liquid purge is required to reject primarily alkane and ester side products, with some corresponding loss of methanol and ethanol. Heat integration between both the reactor and splitter column feeds and reactor effluent is considered for reduction of charge heater and column reboiler duties.

With liquid recycle, the overall carbon conversion is 98% with 22% selectivity to isobutanol. The expected production of isobutanol is 92 MT/day from 500 MT/day of methanol and 172 MT/day of ethanol feed. An additional 13 MT/day of isobutryaldehyde intermediate is recovered in the liquid product and vent streams. This material is considered to have the same value as isobutanol in one economic evaluation case, since it is conceivable that buildup of the C_4 aldehyde in the liquid and gas recycle loops would lead to its eventual conversion to the desired product.

Vent Loss Study

The effect of varying separator temperature has been examined in detail, since increasing this temperature above 100^{0}F (5^{0}F approach to cooling water temperature) would reduce the amount of light byproducts in the liquid recycle stream and consequently the energy costs associated with product fractionation. Excessive separator temperatures, of course, give unacceptably large losses of feed and product in the recycle vent. One initial goal of the process simulation work, therefore, was to find the optimal separator temperature.

Several cases with separator temperatures ranging from 59-180^{0}F were studied to evaluate trends in product losses through the recycle gas and liquid purge streams. The conditions used and results obtained are summarized in Table 2. In each simulation, fresh feed rates were adjusted to obtain the 20300 BPSD combined feed flow upon which the economic evaluation was based. For separator temperatures $>$150^{0}F, fresh feed rates substantially higher than the 5300 BPSD base case were possible since the liquid recycle stream was significantly reduced. In fact, the 150 and 180^{0}F separator temperature cases assumed no liquid purge since all unwanted side products were vented and therefore did not accumulate appreciably in the liquid recycle loop. Losses of feed methanol out the recycle gas vent under these conditions, however, exceeded 3% of that charged to the reactor, as depicted in Figure 2. Other process parameters which were maintained constant in each simulation case were the molar methanol/ethanol ratio (7/1) and H_2 partial pressure ($<$29 psia) in the combined feed. The importance of preserving these values was demonstrated experimentally in the process optimization work. When considering the effect of separator temperature on combined gas and liquid purge stream losses, the optimal value, giving a minimum of combined losses, was found to be approximately 120^{o}F, as illustrated in Figure 3. Therefore, the material balance used for the economic analysis, given in Table 3, was based in this separator temperature.

Economic Analysis

Overview of Methodology

The combination of experimental performance data, the capital cost estimate, and the process simulation provided the basis needed to examine the economic viability of isobutanol synthesis from methanol and ethanol. The base case for economic analysis, therefore, used the best pilot plant results, the 5.9 million dollar initial capital estimate for a 20300 BPSD combined feed stand-alone unit, and the material balance given by the process simulation model at the optimal separator temperature. To complete the economic study, estimations of all operating costs (utilities, fixed costs, working capital, depreciation, and capital expenses) were required in addition to the current market feed and product costs. Isobutanol could be valued as a solvent or an MTBE precursor, the latter material having a significantly lower value but vastly broader market. Furthermore, a number of hypothetical cases were examined to quantify the benefit of improved selectivity to isobutanol. The most realistic of these was the incremental increase in isobutanol yield associated with complete hydrogenation of the intermediate isobutryaldehyde.

Utility and Other Operating Costs

In addition to the material balance, the Hysim software also provided an energy balance for the process model, allowing estimation of utility costs. A summary of major utility streams, with a description of where each utility is needed, the type of utility used, and the power required, is given in Table 4. The assumptions used in calculating these utility requirements, which include widely-accepted pump efficiencies, air cooler fan efficiencies, cooling water and air temperature approaches, and air cooler pressure drops, are given in Table 5. Electrical power was assumed for the feed pump, reactor effluent air cooler, recycle gas compressor, splitter column overhead (air cooled) condenser, and liquid recycle pump. The UOP cost basis for electricity is currently $0.05 per kilowatt-hour. Fuel gas, valued at $2.10 per million BTU, was considered for the feed preheater. Medium pressure (300 psig) steam, costing $3.05 per thousand pounds, was assumed the heat transfer medium for the splitter charge heater and reboiler. Of the three utilities used, the steam represented by far the largest cost. The standard UOP utility cost basis is presented in Table 6. Annual utility cost calculations for the base case isobutanol synthesis plant are shown in Table 7. In addition to utilities, the general economic assumptions used to estimate fixed costs, total plant investment, working capital, depreciation, and capital expenses, are given in Table 8.

Base Case Economic Study and Other Cases Considered

Using the fixed and variable production cost estimations outlined above, a complete economic summary for the base case (Case I) is presented in Table 9. In the section describing feed costs and product revenues, a fuel gas credit is taken for the large amounts of H_2, CO, and CO_2 byproducts generated. Also, isobutanol is valued as a solvent ($903/MT), even though the expected 1998 U.S. consumption at this price is only 54,500 MT. Methanol and ethanol are both assumed to cost $150/MT, which would take into account current levels of U.S. Government subsidies for ethanol. Even under these favorable circumstances, the total feed stock costs ($33.63 MM/year) exceed product revenues ($28.85 MM/year). When all fixed and operating costs are considered, a negative cash flow of $16.5 MM/year is implied for the base case, due to the poor selectivity to isobutanol.

In an actual isobutanol synthesis plant, the intermediate isobutyraldehyde might be hydrogenated to the desired alcohol, giving a more favorable product yield. For this situation (Case II), isobutanol selectivity increases from 22.2 to 26.1%, based on feed carbon. The fuel gas credit, utility, and other costs remain comparable to the base case. If the catalyst and process parameters could eventually be improved to give 50% isobutanol selectivity (Case III), the expected fuel gas make would be reduced 30% and the utilities would be about 50% of the base case requirements. For comparative purposes, the final investigation (Case IV) assumes 100% selectivity to isobutanol, no fuel gas production, and a 75% reduction in utilities compared to the base case. A summary of the cases studied for economic purposes, along with the implications at each condition, is given in Table10. Comparative product revenues, utility costs, and the isobutanol sale price needed to achieve 20% internal rate of return (IRR) on the capital investment, are shown for each case in Table 11. A graphical representation of product price required for 20% IRR versus feed carbon selectivity to isobutanol, is given in Figure 4.

Conclusions of the Economic Analysis

Because of the low selectivity (22%) of the methanol conversion catalyst to isobutanol, the process is uneconomical, even if the isobutanol is valued as a solvent ($903/MT) and not as isobutylene for MTBE production ($352/MT). If the intermediate isobutryaldehyde is considered the same as isobutanol (valid if the aldehyde in liquid recycle of the commercial plant is hydrogenated), 26% selectivity to isobutanol can be achieved. Still, a selectivity of greater than 40% is needed for a 20% internal rate of return on the capital investment. The expected 1998 U.S. isobutanol consumption for solvent and other applications is 54,500 MT. A selectivity of at least 80% would be required for 20% IRR if isobutanol value is based on its gasoline (MTBE precursor) use. This market (10.6 million MT 1997 U.S. estimate) is substantially broader than the solvent market, and therefore a more reasonable basis for the economic analysis.

In summary, based on the experimentally investigated conditions and performance data, this particular process for the conversion of lower alcohols to higher branched oxygenates cannot produce isobutanol at a price which would allow penetration into the gasoline market. Therefore, no competition to the current state-of-the-art TBA byproduct dehydration route to isobutylene is provided. UOP does not intend to continue pursuing this technology further.

REFERENCES

1) P. T. Barger and B.C. Spehlmann, DOE Quarterly Report No. 18, (1995).

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APPENDIX I

CAPTIAL COST ESTIMATE
OF
ISOBUTANOL SYNTHESIS PLANT
(5300 BPSD FRESH FEED)

RC/CF: MKT/NA, EST-B, EST-Q, MKT/Services-DP,MKT/Services-Guildford, KPMcCormick(Delhi), Modular Systems

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UOP *Memorandum*

Date: November 20, 1995

To: Ben Spehlmann

From: Cost Engineering

Subject: **DOE PROJECT**

Proposed Isobutanol Synthesis
Approximate Capital Cost No. 95125
Re: Your Memo Dated October 25, 1995
728008-15

We are noting the preliminary curve-type Capital Costs (based on U.S.A. Gulf Coast erection to UOP Standards) for the units as described below, exclusive of offsites. The estimated costs given below are on an open shop (non-union) labor basis.

Unit

Penex Unit

Fresh Feed, BPSD	5300
Combined Feed, BPSD	20,300
Sep. Press. PSIG	450
H2/Hr	1.0
Makeup Gas Compressor	Not Included
Makeup Gas Driers	Not Included
Feed Driers	Not Included
Stabilizer	Included
Off Gas Scrubber	Not Included

Approximate Capital Cost - Class C (±30%)

Penex Unit, M+L - $MM	$4.4
DE+CE $MM	1.5
Estimated Erected Cost	$5.9MM

D.L. Oak

Date: November 20, 1995
To: Ben Spehlmann
Subject: DOE Project

Please find below a list of items not included in our curve cost estimates along with a list of our assumptions regarding economic conditions. It is important that these lists be given to the recipient of this estimate. The recipient could then understand UOP's scope and basis, as well as those project specific costs not addressed by our curves. This knowledge enables the recipient to select from, and make allowances for, those additional items that are applicable to this specific project. Cost Estimating is available to provide support for both the cost numbers and the estimate's scope and basis.

ITEMS NOT INCLUDED IN UOP COST ESTIMATES OF BATTERY LIMIT COSTS, UNLESS SPECIFIED AS INCLUDED:

1. Cost of land, site preparation, and soil investigation
2. Piling or any unusual foundation requirements
3. Docks, marine terminals, or jetties
4. Access roads to site
5. Home Office Administration Building
6. Worker's transportation allowance, employee housing, worker's barracks, canteens, and recreation facilities
7. Overtime pay during construction
8. Know-how fees and royalties on licensed processes
9. Owner's expenses in developing the project
10. Local permits, taxes and fees, or specific costs of doing business in the area
11. Items concerned with export shipments, such as ocean freight, export crating, marine insurances, import taxes and customs
12. Operating capital and investment in goods in the process
13. Escalation on materials and labor due to price fluctuation or economic conditions
14. Contingencies
15. Cost of startup including testing, manpower, utilities, operating manuals and training programs
16. Spare parts, special tools or maintenance equipment
17. Catalyst, chemicals and raw materials including initial fills or inventories
18. Customer or national standards or codes
19. Special pollution or noise control facilities
20. Electrical main substations
21. Power generation
22. Water or hydrocarbon pipelines
23. Additions or extension to utilities systems or offsites
24. Laboratory facilities or supplies
25. Special communications or computer systems

Date: November 20, 1995
To: Ben Spehlmann
Subject: DOE Project

THE FOLLOWING ASSUMPTIONS ARE NORMALLY MADE REGARDING ECONOMIC CONDITIONS AT THE TIME THE JOB IS BID:

1. There will be an adequate supply of skilled labor available for construction.
2. There will be a reimbursable contract with a fixed cost for Home Office services.
3. The plant will be constructed in the U.S. Gulf Coast.
4. There is no lost time due to climatic conditions.
5. Material and labor prices are based on the date of the estimate.

MODELLING OF HIGHER ALCOHOL SYTHESIS FOR DOE

Conditions for Simulation of Methanol Conversion to Isobutanol, Based on Pilot Plant Data

Temperature, °C	325
Pressure, psig	300
MeOH LHSV, hr-1	1
MeOH/EtOH, molar	7
MeOH/N2 (H2), molar	0.5

Assumptions:

1. C5+ Alcohols are treated as C5's
2. "Other" Aldehydes and Ketones are treated as C5's
3. "Other" Esters are treated as C6's
4. "Other" Hydrocarbons are treated as C6's

Ethanol ---------- (MeAcetate, n-C3OH, MeBuEther, Me i-Butryate, n-C4OH, i-C4OH, C5+ OH, i-C4 Aldehyde, "Other" Aldehydes and Ketones, "Other" Hydrocarbons)

Methanol -------- (CO, CO2, DME, MeFormate, MeAcetate, C1-C5 HCBN's, n-C3OH, MeBuEther, Me i-Butryate, i-C4OH, C5+ OH, i-C4 Aldehyde, "Other" Aldehydes and Ketones, "Other" Hydrocarbons)

Methanol Conv, % 55.18
Ethanol Conv, % 96.95

	% Methanol Conversion	100% Conv Basis	% Ethanol Conversion	100% Conv Basis
Unconverted	44.82		3.05	
CO	12.09	21.91		
CO2	17.48	31.68		
n-C3OH	0.44	0.80	3.07	3.17
n-C4OH			0.40	0.41
i-C4OH	7.29	13.21	38.96	40.19
C5+ OH	0.67	1.21	9.40	9.70
DME	0.87	1.58		
MeBuEther	0.01	0.02	0.16	0.17
i-C4 Aldehyde	1.55	2.81	8.47	8.74
"Other" Ald + Ketone	0.19	0.34	2.60	2.68
MeFormate	0.32	0.58		
MeAcetate	1.18	2.14	8.26	8.52
Me i-Butyrate	1.50	2.72	21.01	21.67
"Other" Esters			4.62	4.77
C2	0.61	1.11		
C3	0.20	0.36		
C5	0.01	0.02		
Other HC	10.77	19.52		
Total	100.00	100.00	100.00	100.00

	C	H	O
Methanol	1	4	1
Ethanol	2	6	1
CO	1		1
CO2	1		2
n-C3OH	3	8	1
n-C4OH	4	10	1
i-C4OH	4	10	1
C5+ OH	5	12	1
DME	2	6	1
MeBuEther	5	12	1
i-C4 Aldehyde	4	8	1
i-Pentanal	5	10	1
MeFormate	2	4	2
MeAcetate	3	6	2
Me i-Butyrate	5	10	2
Et i-Butyrate	6	12	2
C2	2	6	
C3	3	8	
C5	5	12	
C6	6	14	

Reaction Coefficients for HYSIM Simulation:

Methanol	-100	
Ethanol		-100
CO	21.91	
CO2	31.68	
n-C3OH	0.27	2.11
n-C4OH		0.21
i-C4OH	3.30	20.09
C5+ OH	0.24	3.88
DME	0.79	
MeBuEther	0.00	0.07
i-C4 Aldehyde	0.70	4.37
i-Pentanal	0.07	1.07
MeFormate	0.29	
MeAcetate	0.71	5.68
Me i-Butyrate	0.54	8.67
Et i-Butyrate		1.59
C2	0.55	
C3	0.12	
C5	0.00	
C6	3.25	
H2	138.8	37.27
H2O	6.26	36.32
C Balance:	100.00	100.02
H Balance:	100.00	100.00
O Balance:	100.00	100.00

Gas Distribution (Molar):

@55.18/96.95 MeOH/EtOH Conversions

	Calc:	at Equil:	Actual:
H2	62.29	67.40	71.30
H2O	21.37	16.26	3.70
CO	6.68	2.11	10.21
CO2	9.66	14.23	14.79
Total	100.00	100.00	100.00

Table 2
ISOBUTANOL PLANT PERFORMANCE vs SEPARATOR TEMPERATURE

Operating Conditions		"Best" Pilot Plant Results	Capital Cost Estimate Basis	Process Simulation →					
Fresh Feed,	BPSD		5300	4980	5050	5090	5220	7120	8580
Combined Feed,	BPSD		20300	20300	20300	20300	20300	20300	20300
Fresh MeOH,	BPSD			3700	3750	3780	3870	5300	6500
Combined MeOH,	BPSD			6430	6550	6640	6840	9140	10580
Fresh MeOH,	KG-MOLES/HR			608	617	622	637	872	1069
Combined MeOH,	KG-MOLES/HR			1057	1078	1092	1124	1504	1740
Total Carbon In	KG-MOLES/HR			900	913	921	943	1290	1540
HPS Temp,	°F			59	80	100	120	150	180
Recycle Gas/Comb Feed,	MOLAR			0.12	0.12	0.12	0.12	0.12	0.12
Recycle Gas/Fresh Feed,	MOLAR		1.0	0.33	0.33	0.33	0.33	0.28	0.24
Methanol/Ethanol,	MOLAR	7.0		7.0	7.1	7.1	7.1	7.0	7.1
H_2 Partial Pressure,	PSIA	<29		26	26	25	25	25	24
Performance Data									
Carbon Conversion,	%			97.0	97.5	97.8	98.3	96.7	92.8
Isobutanol Selectivity,	%			22.1	22.2	22.1	22.1	22.2	22.1
Isobutanol Yield*,	%			21.5	21.6	21.6	21.5	21.2	19.7
Feed and Product Losses, Carbon % of Fresh Feed									
VENT LOSSES									
Methanol				0.3	0.5	0.8	1.3	3.2	7.1
Ethanol				0.0	0.0	0.0	0.0	0.1	0.1
Isobutanol				0.0	0.0	0.0	0.1	0.3	0.8
LIQUID PURGE LOSSES									
Methanol				2.6	1.9				
Ethanol				0.0	0.0				
Isobutanol				0.0	0.0				
TOTAL				2.9	2.4				

*NOTE: ISOBUTANOL LOST TO VENT IS SUBTRACTED FROM THE TOTAL YIELD

Table 3

DOE ISOBUTANOL SYNTHESIS CASE

HYSIM (V2.50) - Generated Material Balance for 120 F Separator Case

	Feed Kg-Moles/hr		Product Kg-Moles/hr					
	Methanol	Ethanol	Recy Vent	Liq Purge	Ovd Vapor	Liq Product	Recy Liq	Recy Gas
Methanol	650		12.4	4.0	0.2		494.7	2.3
Ethanol		156	0.1				4.8	
Isobutanol			0.2			52.0	0.5	

C Conv:	98.3
IC4OH Sel:	22.1

TOTAL IN: PER DAY	Metric Tons	672	**TOTAL OUT: PER DAY**	Metric Tons	673
	Kg-Moles C	23095		Kg-Moles C	23121
	Kg-Moles H	84884		Kg-Moles H	84935
	Kg-Moles O	19347		Kg-Moles O	19358

	C	H	O	Recy Vent	Liq Purge	Ovd Vapor	Liq Product	**MOLES C**	**MOLES H**	**MOLES O**
Methanol	1	4	1	9.55	3.08	0.17	0.00	400	1598	400
Ethanol	2	6	1	0.08	0.04	0.00	0.00	6	17	3
Hydrogen		2		49.49	0.00	0.12		0	49231	0
CO	1		1	32.81	0.00	0.10		1175	0	1175
CO2	1		2	304.09	0.16	2.05		6961	0	13922
n-C3OH	3	8	1	0.92	0.82	0.02	5.89	382	1019	127
n-C4OH	4	10	1	0.01			0.57	31	78	8
i-C4OH	4	10	1	0.39	0.01	0.00	92.48	5015	12538	1254
C5+ OH	5	12	1	0.02			15.98	908	2180	182
DME	2	6	1	5.38	0.10	0.05		240	721	120
MeBuEther	5	12	1	0.24	0.05	0.00	0.01	17	41	3
i-C4 Aldehyde	4	8	1	12.50	3.67	0.18	2.58	1051	2101	263
i-Pentanal	5	10	1	0.01			4.35	253	507	51
MeFormate	2	4	2	2.48	0.15	0.03		89	177	89
MeAcetate	3	6	2	21.37	2.51	0.29	0.00	[redacted]	1958	653
Me i-Butyrate	5	10	2	1.06	0.16	0.01	40.61	2049	[redacted]	
Et i-Butyrate	6	12	2	0.06			6.84			
C2	2	6		2.50	0.00	0.01				
C3	3	8		0.79	0.00	0.01				
C5	5	12		0.05	0.00	0.00				
C6	6	14		39.59	2.65	0.56	0.00			
Water	0	2	1	2.12	0.92	0.04				
Total				485.49	14.33	3.64	169.34			

Table 4

SUMMARY OF UTILITY STREAMS -- DOE ISOBUTANOL SYNTHESIS PLANT

STREAM	DESCRIPTION	UTILITY	QUANTITY
EN1	Feed Pump Power Delta P=325 psig	Electricity	42.3 KW
EN2	Feed Preheater Delta T=280 F End Temp=617 F	Fuel Gas	44.1 MMBtu/hr
EN3-EN5	Reaction Heat	(Assume Adiabatic)	0
EN6	Reactor Effluent Cooler Delta T=43 F End Temp=120 F	Electricity (Air Cooler)	67.1 KW
EN7	Compressor Delta P=40 psig	Electricity	57.1 KW
EN8	Splitter Overhead Condenser Delta T= 144 F End Temp=170 F	Electricity (Air Cooler)	525 KW
EN9	Splitter Reboiler 398 F Bottoms 366 F Feed	MP Steam	199 Mlb/hr
EN10	Liquid Recycle Pump Delta P=115 psig	Electricity	41.8 KW
EN11	Splitter Charge Heater Delta T=175 F End Temp=366 F	MP Steam	74.6 Mlb/hr

[redacted]

CALCULATION OF UTILITY REQUIREMENTS

#1 Feed Pump

ΔEnthalpy=29.4KW 80% motor eff.
Factor for centrifugal pump=1.15

42.3 KW electric

#2 Feed Preheater

44.1 MM Btu/hr fuel gas

#3 Reactor Effluent Cooler

ΔEnthalpy=9.46 MM Btu/hr

Cooling air ΔT=25°F (95°F inlet, 120°F outlet) 0.453 Btu/ft^3
ΔP=5.4 lb/ft^2, 70% fan eff., 90% motor eff.

67.1 KW electric

#4 Recycle Gas Compressor

ΔEnthalpy=39.7 KW 80% motor eff
Factor for entrifugal pump=1.15

57.1 KW electric

#5 Splitter Overhead Condenser

ΔEnthalpy=221.2 MM Btu/hr

Cooling air ΔT=75°F (95°F inlet, 170°F outlet) 1.36 Btu/ft^3
ΔP=5.4 lb/ft^2, 70% fan eff., 90% motor eff.

525 KW electric

#6 Splitter Reboiler Bottoms

ΔEnthalpy=161 MMBtu/hr

199 Mlb/hr medium pressure (300psig) steam

#7 Liquid Recycle Pump

ΔEnthalpy=29.1 KW 80% motor eff
Factor for centrifugal pump = 1.15

41.8 KW electric

#8 Splitter Charge Heater

60.4 MMBtu/hr [redacted]

74.6 Mlb/hr medium pre[redacted]

Table 6

Utility Costs Basis

Fuel Oil Value	$0.28	per Gallon =====>	$79 per MT
Fuel Oil Gravity	0.9500		
Fuel Oil Heat of Combustion	17,000	BTU/lb	

HP Steam (Superheated) @600 psig and 700 deg F	1352	BTU/lb
MP Steam (Staurated) @150 psig	1194	BTU/lb
LP Steam (Saturated) @50 psig	1174	BTU/lb
Boiler Feed Water @ 60 deg F	28	BTU/lb
Boiler Feed Water @ 250 deg F	219	BTU/lb
Boiler Efficiency	85%	
Boiler Heating Cost as Percent of Total	95%	

Utility	Units	Calculated Value	Recommended Value
Electrical Power	$/KWH	$0.04	$0.05
High Pressure Steam	$/MLB	$3.45 *	$3.45
Medium Pressure Steam	$/MLB	$3.03 *	$3.05
Low Pressure Steam	$/MLB	$2.98 *	$3.00
Boiler Feed Water	$/MLB	$0.42 *	$0.40
Condensate (Credit)	$/MLB	$0.42 *	$0.40
Cooling Water	$/MGal	$0.08	$0.10
Fuel Fired	$/MM BTU	$2.10 *	$2.10
Inert Gas	MSCF	$1.32	$1.35

* Calculated from fuel oil value

[redacted]

CALCULATION OF TOTAL ANNUAL UTILITY COSTS

Electric Power (#1 + #4 + #3 + #5 + #7) = 733.3 KW x 8000 hr x $0.05/KWH

= 0.293 MM$/yr

Fuel Gas (#2) = 44.1 MMBtu/hr x 8000 hr x $2.10/MMBtu

= 0.741 MM$/yr

Medium Pressure(300psig) Steam (#6 + #8)

274 Mlb/hr x 8000 hr x $3.05/Mlb

= 6.68 MM$/yr

Total Utility Costs = 7.71MM$/year

[redacted]

Table 8

Basis for Economic Calculations

Fixed Costs	
Staffing	4.8 Operators/Position
Operator Salaries	$33,000/yr
Supervision	37% Labor
Direct Overhead	45% Labor/Super
Maintenance	3% ISBL*
Plant Overhead	65% Labor/Maint.
Tax & Insurance	1.5% Fixed Inv*

Capital Expenses	
Interest on Capital	None
Interest on Working Capital	10%/yr

Utility	Units	Value
Electrical Power	$/KWH	$0.05
High Pressure Steam	$/MLB	$3.45
Medium Pressure Steam	$/MLB	$3.05
Low Pressure Steam	$/MLB	$3.00
Boiler Feed Water	$/MLB	$0.40
Condensate (Credit)	$/MLB	$0.40
Cooling Water	$/MGal	$0.10
Fuel Fired	$/MM BTU	$2.10
Inert Gas	MSCF	$1.35

Total Plant Investment	
ISBL Investment	Curve Costs
Offsites	30% ISBL*
Interest During Construction	10%/yr* for 3 years
Royalties	Full UOP Rates
Catalyst/Adsorbent Inventory	Capitalized

Working Capital	
Raw Materials Storage	15 days at Delivered Value
Total Products in Storage	15 Days Cost of Production
Accounts Receivable	30 Days Production (Key Products)
Accounts Payable (Credit)	30 Days Production (Raw Materials)
Cash Kept on Hand	7 Days Gross Profit
Noble Metal Inventory	Full Inventory at Market Value (Pt @ $376/tr oz)
Warehouse Inventory	2% ISBL Investment*
Chemicals Inventory	Full Inventory at Markey Value (Solvent, Desorbent, ect...)

Depreciation	
ISBL Depreciation	10%/yr
Offsite Depreciation	10%/yr
Royalty Depreciation	10%/yr
Inventory Depreciation	10%/yr (Composite Account)
Depreciation Schedule	Straight Line

* Parameters designated by an asterisk should not be considered in economic evaluations where two or more cases are compared to each other.

[redacted]

Table 9

BASE CASE METHANOL TO ISOBUTANOL PRODUCTION ECONOMICS

Basis	333.33	days/yr
	8,000	hours/yr

Daily production: 95.1 MT/day

VARIABLE COSTS AND REVENUES

Mass Balance	Units	Units/yr	$/unit	$MM/yr
Main products				
Isobutanol	MT	31,687	903	28.61
Fuel Gas	MMBtu	120,000	2.00	0.24
Total products	**MT**	**31,687**		**28.85**
Feedstocks				
Methanol	MT	166667	150	25.00
Ethanol	MT	57500	150	8.63
Total feedstocks		**224167**		**33.63**

Consumables: catalysts, adsorbents, and chemicals	$/MT	$MM/yr
Catalysts and chemicals	15.77	0.50
Total consumables		**0.50**

Utilities	$/unit	Units/MT	$/MT	$MM/yr
Power, kWh	0.050	185.1	9.255	0.29
Steam (HP), Mlb	3.45		0.000	0.00
Steam (MP), Mlb	3.05	69.18	210.999	6.69
Steam (LP), Mlb	3.00		0.000	0.00
Boiler feed water, Mlb	0.40		0.000	0.00
Condensate, Mlb	0.40		0.000	0.00
Cooling water, MGal	0.1		0.000	0.00
Fuel fired, MMBtu	2.10	11.13	23.373	0.74
Inert gas, m^3	0.045		0.000	0.00
Total utilities			**243.63**	**7.72**

FIXED OPERATING COSTS

				$MM/yr
Labor				
Operators per shift		4.8 @	$33,000 per year	0.76
Supervision	@	37%	of operating labor	0.28
Direct overhead	@	45%	or labor & superv.	0.47
				1.51
Maintenance				
Materials and labor	@	3%	of ISBL investment	0.18
Overhead expenses				
Plant overhead	@	65%	of labor & maintenanc	1.10
Taxes and insurance	@	1.5%	of fixed investment	0.14
				1.23
Other expenses				
Intrst. on capital (debt)	@	0%	per year (100% equity)	
Intrst. wrkng. capital	@	10%	per year	0.21
Product shipping	@	$10	per MT	0.32
Sales and admin.	@	0.2%	of sales	0.06
				0.59

CAPITAL CHARGES

Depreciation and amortization				
ISBL	@	10%	per year	0.68
OSBL	@	10%	per year	0.24
Royalties	@	10%	per year	0.00
Capitalized inventories	@	10%	per year	0.00
				0.92

CAPITAL ITEMS

Plant investment			$MM
M & L			4.4
DE & CE			1.5
ISBL			5.9
OSBL	@35%	ISBL	2.07
Interest	@10%	2 year	1.23
Total fixed investment			**9.20**
Royalties			
Royalties			0.00
Total royalties			**0.00**
Capitalized inventories			**0.00**
Total plant investment			**9.20**

Working capital			$MM
Feedstock storage	15	days	1.51
Main product storage	15	days	1.29
By-product storage	15	days	0.00
Accts. receivable	30	days	2.60
Accts. payable	30	days	(3.03)
Cash in hand	7	days	(0.35)
Spares	2%	ISBL	0.12
Total working capital			**2.14**
Cats., adsorbs., and chems. inventory			
Catalysts			
Chemicals			
Total inventory			**0.00**

ECONOMIC ANALYSIS

	$MM/yr	$/MT	$/lb	%	cents/gal
Gross margin					
Main product sales	28.85	910.57	0.41		264.98
By-product sales					
Minus feedstock cost	33.63	1,061.16	0.48	72.7	308.80
Gross margin	**(4.77)**	**(150.59)**	**(0.07)**		**(43.82)**
Variable costs					
Consumables	0.50	15.77	0.01		4.59
Utilities	7.72	243.63	0.11		70.90
Total variable costs	**8.22**	**259.40**	**0.12**	**17.8**	**75.48**
Fixed costs					
Labor	1.51	47.67	0.02		13.87
Maintenance	0.18	5.59	0.00		1.63
Overhead expenses	1.23	38.97	0.02		11.34
Other expenses	0.59	18.58	0.01		5.41
Total fixed costs	**3.51**	**110.80**	**0.05**	**7.6**	**32.24**
Cash cost of production	**45.36**	**1,431.36**	**0.65**		**416.53**
Cash cost of production for main product	**45.36**	**1,431.36**	**0.65**		**416.53**
Cash flow	**(16.50)**	**(520.79)**	**(0.24)**		**(151.55)**
Capital charges					
Plant depreciation	0.92	29.03	0.01		8.45
Royalty amortization	0.00	0.00	0.00		0.00
Inventory amortization	0.00	0.00	0.00		0.00
Total capital charges	**0.92**	**29.03**	**0.01**	**2.0**	**8.45**
Net cost of production	**46.28**	**1,460.39**	**0.66**	**100.0**	**424.97**
Net cost of production for main product	**46.28**	**1,460.39**	**0.66**		**424.97**
Pre-tax income	**(17.42)**	**(549.82)**	**(0.25)**		**(160.00)**
Simple pre-tax ROI, %	**(189.38)**				
Simple payback, years	**(0.56)**				

DCF IRR, %		**ERR** @	10 years	**ERR** @	20 years
DCF payback, years		**(0.58)** @	20%	**(0.57)** @	10%
Main product sale price, $/MT	20% IRR	1,493.04 @	10 years	1,483.41 @	20 years
	30% IRR	1,517.70 @	10 years	1,511.35 @	20 years
	40% IRR	1,544.08 @	10 years	1,540.06 @	20 years

[redacted]

Table 10

SUMMARY OF CASES USED FOR DOE ISOBUTANOL PLANT ECONOMIC STUDY

($9.2 MM Capital Investment is Assumed for 500 MT/day Methanol Consumption in Each Case)

CASE I, BASE CASE

Assume: Best Results from UOP Research Pilot Plant Work are Obtained Commercially, Isobutanal in the Product Stream has the Same Value as Isobutanol

This Implies:

--22.2% Carbon Selectivity to Isobutanol + Isobutanal Gives 31687 MT/yr Product
--H_2, CO, and CO_2 Byproducts Give 120,000 MMBtu/yr Fuel Gas Credit
--Utilities Costs to Fractionate Liquid Byproducts from Main Product are 7.72 MM$/yr

CASE II

Assume: All Isobutanal Produced is a Reaction Intermediate and Therefore Eventually Converted to the Desired Isobutanol Product

This Implies:

--26.1% Carbon Selectivity to Isobutanol Gives 37137 MT/yr Product
--Same Fuel Gas Credit as the Base Case
--Same Utilities Costs as the Base Case

CASE III

Assume: 50% Selectivity to Isobutanol is Achievable Commercially

This Implies:

--50% Carbon Selectivity to Isobutanol Gives 71264 MT/yr Product
-- Fuel Gas Credit is Reduced 30% from the Base Case
--Utilities Costs are Reduced 50% from the Base Case

CASE IV

Assume: 100% Selectivity to Isobutanol is Achievable Commercially [redacted]

This Implies:

--100% Carbon Selectivity to Isobutanol Gives 142[redacted]
-- No Fuel Gas Credit [redacted]
--Utilities Costs are Reduced 75% from the Base [redacted]

Table 11

BASIS FOR DOE ECONOMIC ANALYSIS

(500 MT per Day Methanol Feed)

CASE NUMBER		I	II	III	IV
Carbon % Selectivity to Isobutanol		22	26	50	100
Feed (Methanol + Ethanol) Requirement	MT/yr	224000	224000	224000	224000
Product (Isobutanol + Isobutanal) Generation	MT/yr	31700	37100	71300	142500
Feed Cost ($150 per MT for both MeOH and EtOH)	MM$/yr	33.63	33.63	33.63	33.63
Utilities Cost	MM$/yr	7.72	7.72	3.86	1.93
Fixed Capital Investment	MM$	9.20	9.20	9.20	[redacted]
Product Sale Price Needed for 20% IRR	**$/MT**	**1490**	**1270**	[redacted]	[redacted]

Figure 1

DOE120#H.SIM

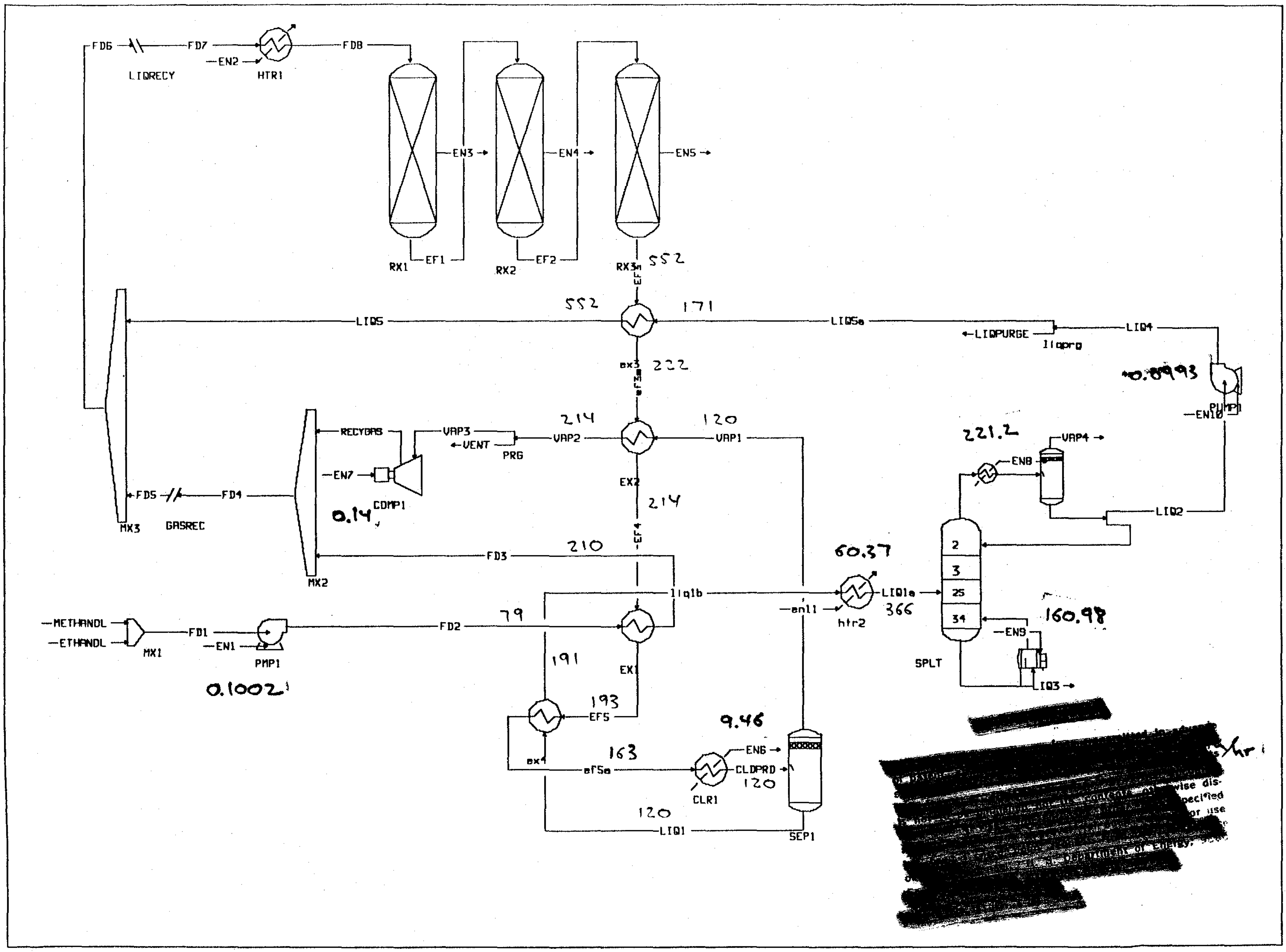
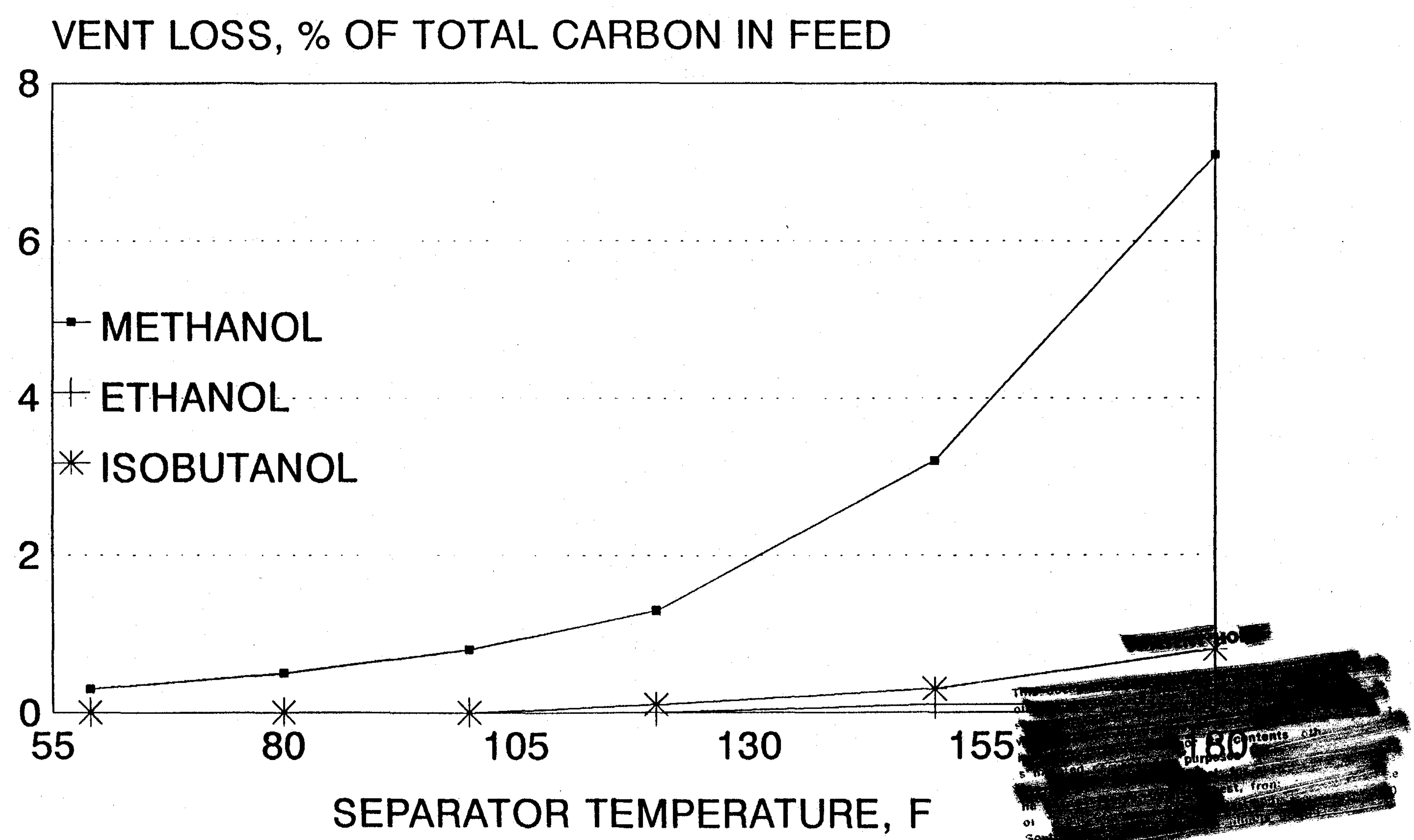


Figure 2

VENT LOSSES vs SEPARATOR TEMPERATURE

DOE ISOBUTANOL SYNTHESIS SIMULATION



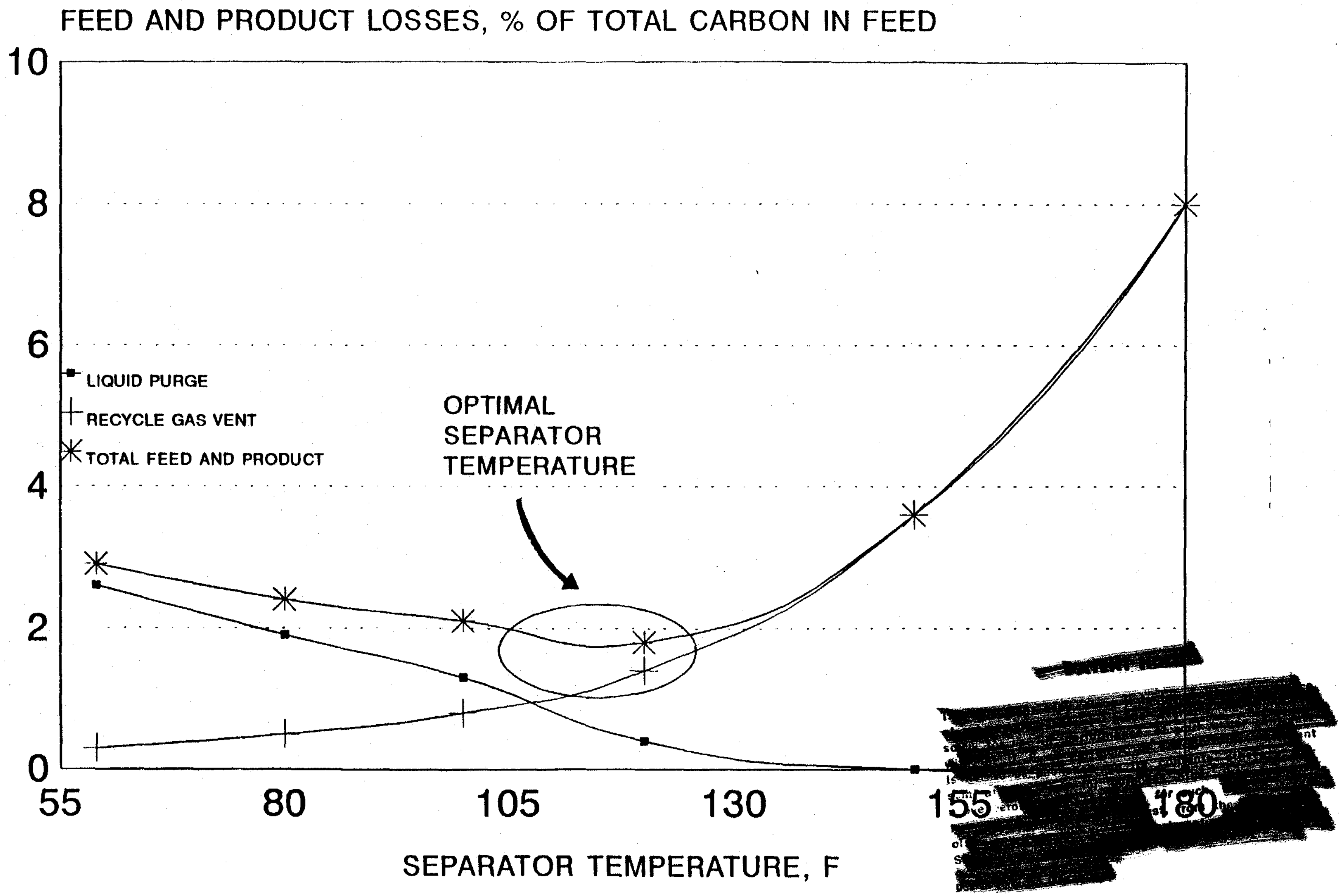
[redacted]

250 psig separator pressure, 7/1 MeOH/EtOH and 25 psia H_2 partial pressure in combined feed

Figure 3

LIQUID PURGE, VENT, AND TOTAL FEED & PROD LOSSES vs SEPARATOR TEMPERATURE

DOE ISOBUTANOL SYNTHESIS SIMULATION

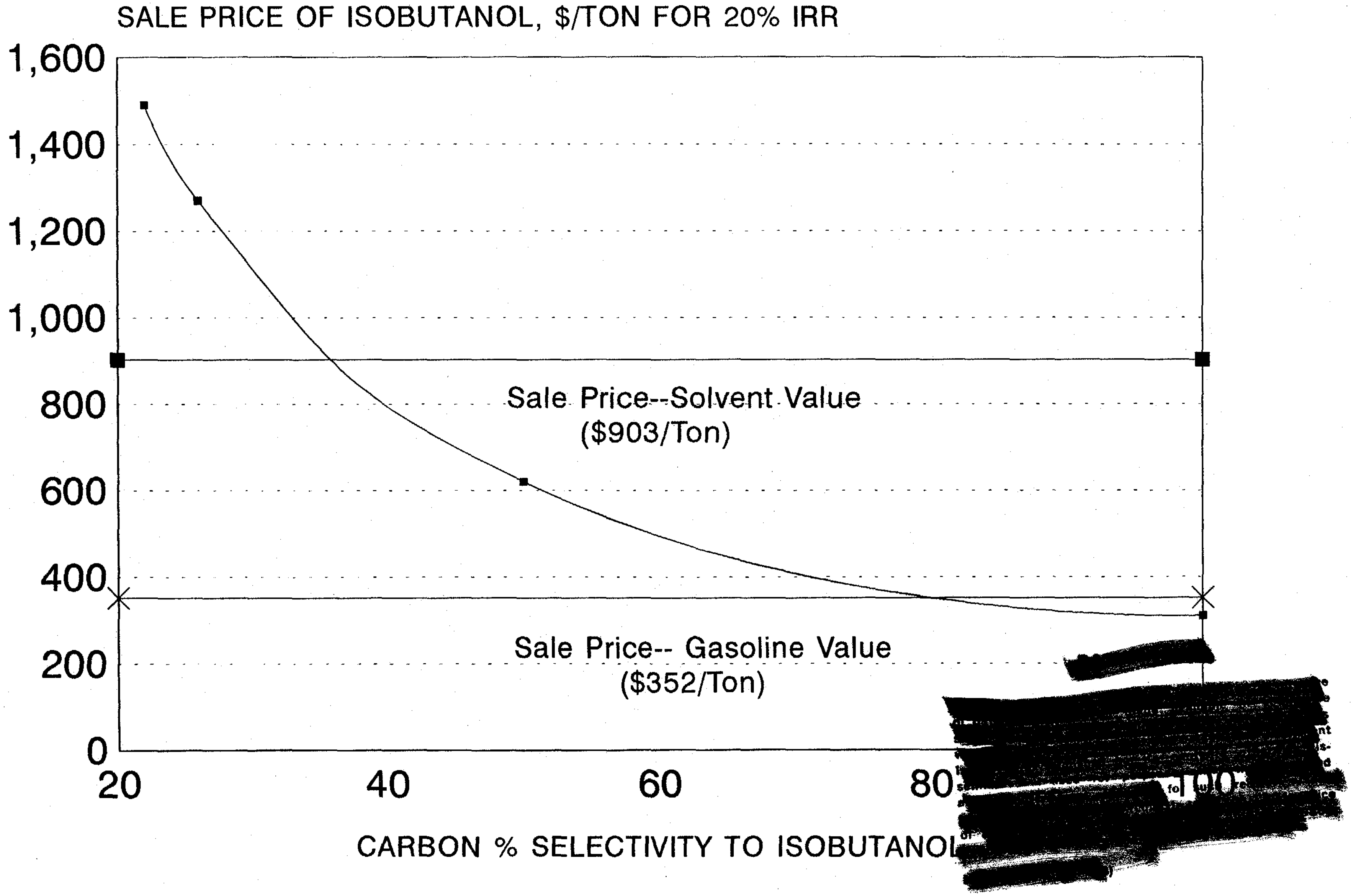


250 psig separator pressure, 7/1 MeOH/EtOH and 25 psia H2 partial pressure in combined feed

Figure 4

PRODUCT PRICE NEEDED FOR 20% INTERNAL RATE OF RETURN vs SELECTIVITY

DOE ISOBUTANOL SYNTHESIS ECONOMICS



[redacted]

Base Case = 22.1% Carbon Selectivity to Isobutanol from Pilot Plant Studies