Date: 12/10/80

Project Title: Fuel Grade Ethanol Recovery by Solvent Extraction

Project No: E-19-628 (subproject is G-33-674/Liotta)

Project Director: Dr. D. W. Tedder

Sponsor: Midwest Research Institute; Solar Energy Research Institute Division

Agreement Period: From 9/15/80 Until 9/14/81

Type Agreement: Subcontract No. XK-0-9082-1 under DOE Prime Contract No. EG-77-C-01-4042

Amount: $35,489
          35,454 (G-33-674)
          $70,943 TOTAL

Reports Required: Monthly Contract Management Summary Reports; Monthly Technical Progress Reports; Semi-Annual Topical Report; Final Technical Report

Sponsor Contact Person (s):

Technical Matters

Dr. Larry Douglas
Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401
   303/231-1470

Contractual Matters
(thru OCA)

Mr. F. C. Brooke
Subcontract Administrator
Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401
   303/231-1123

Defense Priority Rating: None

Assigned to: Chemical Engineering   (School/kabxxanxyy)

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date __November 7, 1985__

Project No. __E-19-628__   School/XXX __Chemical Engineering__

Includes Subproject No.(s) __G-33-674, G-33-609, E-19-621__

Project Director(s) __D.W. Tedder__   GTRC /XXXX

Sponsor __Solar Energy Research Institute__

Title __Fuel Grade Ethanol Recovery by Solvent Extraction__

Effective Completion Date: __9/14/82__   (Performance) _____ (Reports)

Grant/Contract Closeout Actions Remaining:

[ ] None

[X] Final Invoice XXXXXXXXXXXXXXXXX and   Statement of Costs—Need
                                           Cumulative on Subcontract XK-0-9082.

[ ] Closing Documents

[X] Final Report of Inventions — *Already submitted under E-19-621.

[X] Govt. Property Inventory & Related Certificate

[ ] Classified Material Certificate

[ ] Other _____

Continues Project No. _____   Continued by Project No. _____

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GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA. GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

January 5, 1981

TO: Distribution

FROM: D. W. Tedder

RE: Fuel-Grade Ethanol Recovery by Solvent Extraction: Progress
     and Contract Management Summary Reports for Period of
     September 15 through December 31, 1980
     SERI # XK-0-9082-1
     GTRI # E-19-628 and G-33-674

Please find the attached reports for this period. We are currently
very optimistic that a suitable extractant can be found among the
class of high boiling alcohols, but the screening tests for alter-
natives are continuing.

                    Sincerely,

                    D. William Tedder
                    Project Director

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Fuel-Grade Ethanol Recovery by Solvent Extraction:
Progress Report for September 15 through December
31, 1980

D. W. Tedder and C. L. Liotta*
Georgia Tech Industrial Separations
Laboratory
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

During this period, progress was made in the development of improved
analytical techniques for quick scouting tests, the utilization of these
techniques for a number of candidate extractants, and the experimental
identification of solvent characteristics that are useful for the recovery
of absolute alcohols in general, and ethanol in particular. The best extract-
ants that have been identified experimentally so far are high-boiling
alcohols. Mixed isomers of tridecanol are commercially available from
Union Carbide Corp., inexpensive, relatively non-toxic, and appear highly
workable in the conceptual recovery system. However, the scouting tests
for alternative extractants better than tridecanol are still continuing.

Considerable effort was expended during this period to develop im-
proved methods for quickly scouting extractant alternatives. During the
early stages of the research effort, these scouting tests are essential in
order to quickly screen a large number of alternatives. The method that has
finally evolved consists of simple test tube equilibrations, visual obser-
vations, and measurements of refractive indices for the phases before and
after equilibration.

*School of Chemistry, Georgia Institute of Technology

Visual observations rapidly indicate solvent performance. For example, the organic volumes increase significantly while the aqueous volumes decrease whenever appreciable quantities of alcohol and/or water extract. Also, those solvents which primarily extract water become hazy upon equilibration, whereas alcohol extraction alone results in a clear organic phase.

If the refractive indices for each phase are measured before and after equilibration, then qualitative and semi-quantitative conclusions can be quickly drawn. For the solvent systems and alcohol mixtures that have been examined, the aqueous refractive index is less than that of the organic before and after equilibration. Moreover, the observed changes in indices have always fallen into one of the categories (or cases) that are shown in Table 1 along with the resulting inferences. This information, together with the visual observations, is sufficient to determine whether or not a candidate extractant should be evaluated further.

If a solvent passes the scouting tests, then it is subjected to a more detailed evaluation in which the apparent distribution coefficients for water and ethanol are measured over a range of aqueous ethanol concentrations. In this case, measured volumes and weights of the solvent are equilibrated with stock alcohol solutions. Phase disengagement times, changes in volumes, weights, and refractive indices are noted, and NMR samples are taken for the calculation of alcohol content. The solvent is then stripped using a specially designed apparatus in the ISL. The alcohol/water product is weighed and an NMR sample is taken for calculating alcohol content in the product. This procedure permits the calculation of distribution coefficients, separation factors, and pseudo y/x equilibrium curves for direct comparison with the vapor/liquid equilibrium curve for ethanol and water.

Currently, the alcoholic content of an aqueous phase is measured using NMR techniques. This method appears reliable for aqueous samples, but it is relatively slow. We hope to alleviate this problem in the near future, however, by switching to a gas chromatographic method for alcohol and water measurements. Ultimately, we hope to utilize a high-pressure liquid/solid chromatograph (HPLSC) for the thermodynamic measurements during the second year of the program. In order to calculate stability constants, solvent

Table 1. Commonly observed refractive changes during scouting tests.

| | Refractive Index Changes[a] | | Conclusions |
Case	Aqueous	Organic	
1	0	0	No phase transfer occurred
2	0	-	Equal amounts of water and alcohol extracted
3[b]	-	-	More ethanol than water extracted
4[c]	+	-	More water than ethanol extracted and/or the solvent is water soluble
5	+	0	The solvent is water soluble, but does not extract

[a]All cases are subject to cancellation of changes, or else change reversals, due to high solvent solubilities in the aqueous phases. In these cases, the aqueous phase is hazy after equilibration or else becomes hazy when it is subsequently diluted with water.

[b]This is the most favorable case.

[c]This case is ambiguous.

concentrations must be measured also.

The following extractant systems have been studied: tri-n-butyl phosphate, tri-neopentyl phosphate, tri-2-ethylhexyl phosphate, dibutyl-butyl phosphonate, diisopropyl benzene, tri-laural amine, tri-cresyl phosphate, and several aniline species. In addition, solvent effects have been examined for n-dodecane, diisopropyl benzene, and dichlorobenzene.

Many of the above extractants were examined in order to test the hypothesis that water extracts by dimerization mechanisms, whereas ethanol can extract (theoretically) as a one-to-one complex. This hypothesis still seems valid. Unfortunately, ethanol forms a hydrate which must be destroyed in order for the resulting "free" ethanol to extract as a one-to-one organic complex. Therefore, solvents that cannot form water dimers extract appreciable amounts of ethanol when the aqueous phase is predominantly ethanol, but practically nothing extracts when the aqueous phase is slightly alcoholic and virtually all of the ethanol exists as a hydrate in the aqueous phase.

On the other hand, high-boiling alcohols may be useful extractants for ethanol recovery, but the mechanism may be somewhat different. In this case, the solvent is chosen to preferentially extract the ethanol-water hydrates, rather than water alone. Subsequently, the ethanol is selectively stripped while the water forms a second liquid phase that settles below the solvent.

In order to test this second approach, several scouting tests were completed for solvents including 2-ethylhexanol, isodecanol, and Umbrex-n-fatty alcohol. All of these solvent systems appear highly favorable, relative to the phosphonates, phosphates, etc. mentioned above, but tridecanol seems to be the most attractive among these four candidates. In fact, the scouting tests suggest that tridecanol may be used with organic-to-aqueous flow ratios perhaps as low as two or three. If this preliminary interpretation is correct, then tridecanol is a much more favorable extractant than the assumed design basis extractant, 30% TBP in dodecane, which was assumed to operate with an organic-to-aqueous flow ratio of ten. Consequently, the tridecanol system may yield more favorable economics and reduced energy demand than was estimated in the initial research proposal for this program which was based on the TBP system.

The only apparent problem with tridecanol at this time are excessively

high disengagement times when the aqueous phase contains more than 40 wt % ethanol. However, a pulse column could be expected to produce a larger droplet size distribution than the separatory funnel tests by reduced pulse frequency and a careful cartridge choice. Alternatively, this problem can be easily overcome through the use of centrifugal contactors for the scrub section of the extraction cascade.

When high-boiling alcohols such as tridecanol are used as extractants, then the water in the organic phase is partly solvated by the presence of the ethanol. However, the water tends to cause the ethanol to enter the organic phase and the water is more tightly bound to the extractant through hydrogen bonding. That is, the ethanol is presumed to have followed the water into the organic as part of the hydrate which subsequently acts as a solvating agent for the water. However, once the organic phase has been separated from the aqueous, it becomes possible to break up the water-ethanol complex through a selective vaporization of the ethanol. The more tightly bonded water molecules tend to agglomerate and reform the aqueous phase as ethanol is stripped by vaporization. Under these circumstances, the ethanol may be selectively stripped from the solvent while the water remaining in the solvent is centrifuged and recycled back to the extraction cascade. Hence, the stripping configuration will involve several stages and a recycle stream that was not previously identified. These changes, however, appear minor and the overall stripping characteristics for tridecanol appear somewhat more favorable than those which were assumed earlier for the TBP system. That is, stripping can probably be carried out economically at higher pressures and with more water in the solvent than was assumed earlier.

During the next quarter, we expect to develop a more precise understanding of the tridecanol system by continuing our batch equilibrations and stripping tests for a range of alcohol and water concentrations. In addition, scouting tests will be completed for several secondary and tertiary aliphatic alcohols, diols, and possible triols. We will also test tertiary amine oxides and aliphate sulfoxides. We will also begin a cross-current experiment to simulate the tridecanol extraction cascade if the results continue to look favorable.

We have also received a set of blueprints for an eight stage bank of

Savannah River type high-speed centrifugal contactors from friends at Argonne National Laboratory. A bank of contactors is now being constructed in the Chemical Engineering Machine Shop at Georgia Tech. We hope to have the bank operating no later than the end of next summer. In this case, it should be possible to complete the engineering evaluations that were originally planned for this program, if we also receive the requested equipment grant from the Georgia Tech Research Institute (GTRI). This grant will provide funds to purchase the high-pressure liquid/solid chromatograph, flow control equipment for the cascade, a chemical fume hood (which is not really required if tridecanol is used) and, possibly, a bank of mini-mixer-settlers. We hope to have a favorable response from GTRI in the near future.

The GTRI is also continuing negotiations with several companies that are interested in the solvent extraction technology when it is reduced to practice. We are optimistic that additional solvent extraction equipment and expertise may become available to the ISL through this negotiation process. The participating company may also sponsor pilot plant evaluations of the completed system, perhaps during the third year of the research program. Conceivably, a pilot plant demonstration could occur successfully during the latter half of the second year if tridecanol and/or another similar solvent system continues to appear favorable.
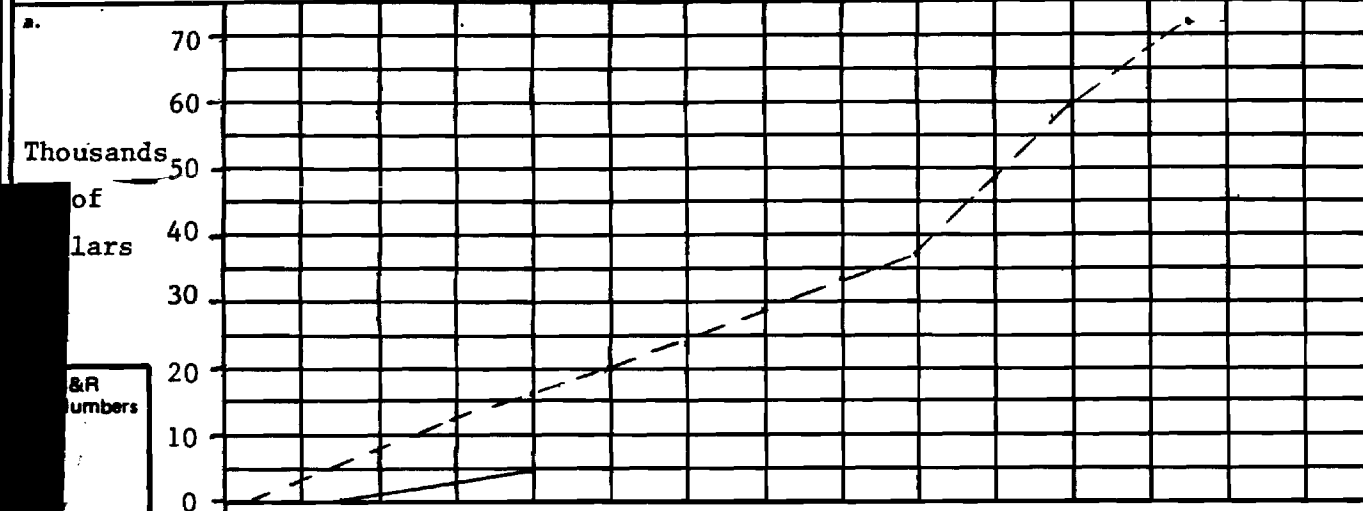
U.S. DEPARTMENT OF ENERGY
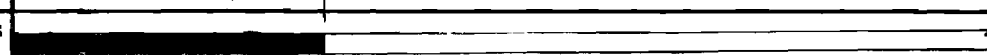
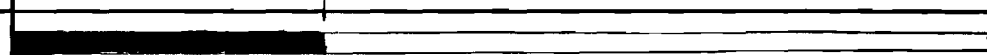# CONTRACT MANAGEMENT SUMMARY REPORT

FORM DOE 536
(1/78)

FORM APPROVED
OMB NO. 38R-0190

1. Contract Identification	2. Reporting Period	3. Contract Number
Fuel Grade Ethanol Recovery by Solvent Extraction	8/15/80 through 12/31/80	XK-0-9082-1

4. Contractor (Name and Address)	
Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, GA 30332	5. Contract Start Date 8/15/80
	6. Contract Completion Date 8/15/81

7. Months	S	O	N	D	J	F	M	A	M	J	J	A	S			8. FY 81

9. Cost Status

a.

Thousands of Dollars

70 60 50 40 30 20 10 0

&R Numbers

g. Cost Plan Date	NA
h. Planned Costs Prior FYs	NA
i. Actual Costs Prior FYs	NA
j. Total Estimated Costs for Contract	70,943
k. Total Contract Value	70,943
l. Unfilled Orders Outstanding	NA
m. Estimate for Subsequent Reporting Period	

		S	O	N	D	J	F	M	A	M	J	J	A	S		
ued s	c. Planned	3.0	4.2	4.3	4.3	4.2	4.3	4.3	4.3	4.3	11.3	11.3	8.2	2.9		
	d. Actual	0.3	1.5	1.6	1.5											
	e. Variance	2.7	2.7	2.7	2.8											
	f. Cum. Variance	2.7	5.4	8.1	10.9											

Manpower Status (Direct Labor)

	e. Manpower Plan Date
	f. Planned Manpower Prior FYs
	g. Actual Manpower Prior FYs
	h. Total Estimated Manpower for Contract
	i. Total Contract Manpower

n-wer	b. Planned														
	c. Actual														
	d. Variance														

Major Milestone Status

Phosphate Synthesis	▼
Alternates Synthesis	
Scoping Tests	
Batch Tests	▽
Equipment Set Up	▽
Continuous Tests	
Solvent Selection	▽

12. Remarks

13. Signature of Contractor's Project Manager and Date

14. Signature of Government Technical Representative and Date
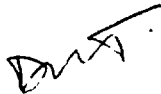
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA. GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

MEMORANDUM   February 6, 1981

TO: Distribution

FROM: D. W. Tedder

SUBJECT: Fuel-Grade Ethanol Recovery by Solvent Extraction: Progress
           and Contract Management Summary Reports - SERI #XK-0-9082-1,
           GTRI #E-19-628 and G-33-674

     Please find the attached reports for this period. Thank you for
your time and consideration.

DWT/sm

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Fuel-Grade Ethanol Recovery by Solvent Extraction:
Progress Report for January 1 through 31, 1981

D. W. Tedder and C. L. Liotta*
Georgia Tech Industrial Separations Laboratory
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

During this period, several additional solvents were subjected to quick scouting tests, two of the more promising extractants were subjected to equilibration and stripping tests, and several oximes were synthesized for testing. High-boiling alcohols continue to appear promising for gasahol production; however, scouting tests for alternatives are continuing.

Scoping tests were carried out on the following systems: 2-ethylhexanol, tridecanol + bis(2-ethylhexyl) 2-ethylhexyl phosphenate (BEHEHP) (1+1), BEHEHP, BEHEHP + 2 ethylhexanol (1+1), tridodecylamine oxide, and tridodecylamine oxide + 2-ethylhexanol (1+1). The mixed extractants were examined to test a hypothesis that favorable synergisms may exist in these cases. That is, whether or not a phosphonate or amine oxide would preferentially associate with ethanol after the alcohol-water complex had transferred into the organic phase by association with either 2-ethylhexanol or trideconol.

Unfortunately, these scoping test results were negative and our current best candidates are tridecanol and 2-ethylhexanol. Several additional secondary and tertiary alcohols are back ordered for testing and should arrive in the near future.

* School of Chemistry, Georgia Institute of Technology

Two-ethylhexanol and tridecanol were studied more carefully during this period by batch equilibration and stripping test. Both of these alcohols appear to give significant enrichment in ethanol. In fact, some of our products appeared to be nearly 100 wt % ethanol based on density measurements. Subsequently, (about one week later), the alcohol product densities had increased. Therefore, we are now uncertain as to how dry these products actually were.

We have experienced difficulty in measuring our water/alcohol ratios based on density or NMR analysis. Therefore, we have been working on the development of simple tests to permit a rapid evaluation of our alcohol product quality before it has a chance to pick up water. Mixing the product with unleaded gasoline appears attractive in this regard and we have been able to dissolve in excess of 80% of our product in gasoline at a 9:1 gas alcohol product ratio. We are also using GC analysis and are upgrading our procedures for analyzing products immediately after they are produced.

We are happy to report that the Georgia Tech Research Institute (GTRI) has seen fit to grant the ISL $52K in equipment money. We have sent out bids for a new GC and also for a high-pressure liquid chromatograph (HPLC). The GC will aid in rapid measurements of our product quality and the HPLC is needed to establish the ternary phase equilibrium diagrams and perform the necessary thermodynamic studies to better understand the extraction mechanisms.

Construction of the ANL laboratory-scale high-speed centrifugal contactor has not yet started, but we have obtained the necessary stainless steel. We hope to begin machining components next month. Control equipment will be ordered in the near future.

FORM DOE 536
(1/78)

CONTRACT MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 38R–0190

1. Contract Identification	2. Reporting Period	3. Contract Number
Fuel Grade Ethanol Recovery by Solvent Extraction	1/1/81 through 1/31/81	XK-0-9082-1

4. Contractor (Name and Address)
Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, GA 30332

5. Contract Start Date 8/15/80

6. Contract Completion Date 8/15/81

7. Months	S	O	N	D	J	F	M	A	M	J	J	A	S			8. FY 81

9. Cost Status

a. Thousands of Dollars (70, 60, 50, 40, 30, 20, 10, 0)

b. B&R Numbers

g. Cost Plan Date NA

h. Planned Costs Prior FYs NA

i. Actual Costs Prior FYs NA

j. Total Estimated Costs for Contract 70,943

k. Total Contract Value 70,943

l. Unfilled Orders Outstanding NA

Accrued Costs		S	O	N	D	J	F	M	A	M	J	J	A	S			
	c. Planned	3.0	4.2	4.3	4.3	4.2	4.3	4.3	4.3	4.3	11.3	11.3	8.2	2.9			
	d. Actual	0.3	1.5	1.6	1.5	2.8											
	e. Variance	2.7	2.7	2.7	2.8	1.4											
	f. Cum. Variance	2.7	5.4	8.1	10.9	12.3											

m. Estimate for Subsequent Reporting Period

10. Manpower Status (Direct Labor)

a.

Man-power																	
	b. Planned																
	c. Actual																
	d. Variance																

e. Manpower Plan Date

f. Planned Manpower Prior FYs

g. Actual Manpower Prior FYs

h. Total Estimated Manpower for Contract

i. Total Contract Manpower

11. Major Milestone Status

a. Phosphate Synthesis
b. Alternates Synthesis
c. Scoping Tests
d. Batch Tests
e. Equipment Set Up
f. Continuous Tests
g. Solvent Selection
h.
i.

12. Remarks

13. Signature of Contractor's Project Manager and Date

14. Signature of Government Technical Representative and Date

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA. GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

March 13, 1981

TO: Distribution

FROM: D. W. Tedder

RE: Fuel-Grade Ethanol Recovery by Solvent Extraction: February 1981
Contract Management Summary Report and Technical Progress Report
for the Period September 15, 1980 through February 28, 1981
SERI # XK-0-9082-1
GTRI # E-19-628 and G-33-674

Please find the attached reports for this period. Thank you for your
time and consideration.

Sincerely,

D. William Tedder
Project Director

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3/23/81

Fuel-Grade Ethanol Recovery by Solvent Extraction:

February 1981 Contract Management

Summary Report

(SERI No. XK-0-9082-1)

D. W. Tedder and C. L. Liotta*

Georgia Tech Process Design Institute

School of Chemical Engineering

Georgia Institute of Technology

Atlanta, Georgia 30332

During this period a different technique for measuring the distribution coefficients of water and ethanol was examined. With this approach the mutual solubility curve is first titrated using water and ethanol additions to a quantity of the candidate solvent, and then by adding solvent and ethanol to water. Increments are added using burets and the pure component densities are estimated so that the weight fraction of ethanol, water, and solvent along the mutual solubility curve can be calculated. This technique appears to be much more accurate than the previously adopted analytic techniques in which the distribution coefficients are measured directly.

*School of Chemistry, Georgia Institute of Technology

Based on the mutual solubility curve, it appears that the system 60 vol % tridecanol in n-dodecane could be used to obtain a product that is about 94 wt % ethanol. The required organic-to-aqueous flow ratio at the raffinate end of the extraction cascade is only 2.2 rather than 10 as was initially assumed. This result is highly favorable and we are making plans to reevaluate the economics of ethanol recovery with this new extractant.

Kerosene may be used to obtain an ethanol product that is over 98 wt %, but the solubility curve indicates that this solvent does not possess sufficient capacity for ethanol at the dilute end of the extraction cascade. In particular, the ethanol distribution coefficient appears to be around 0.1 when the alcohol weight percentage is less than about 10 %. Consequently, kerosene alone would require an excessive organic-to-aqueous flow ratio and a high reflux ratio in order to adequately dry the product.

On the other hand, we have learned that the system 30 vol % 2-ethyl-1,3-hexane diol in kerosene can apparently be used to recover a product that contains more than 96 wt % ethanol. Also, this modified system appears to have adequate capacity at the dilute end of the extraction cascade. Therefore, it appears as a highly attractive solvent, but we are optimistic that a diol containing only interior (i.e. secondary or tertiary) hydroxyl groups will yield an even drier product.

Kerosene is less expensive than n-dodecane and appears workable as is discussed above. However, we will compare it further with n-dodecane after completing the solubility curve for the latter substance. Even though n-dodecane is more expensive than kerosene as a diluent, its use may be justified if the product quality is improved.
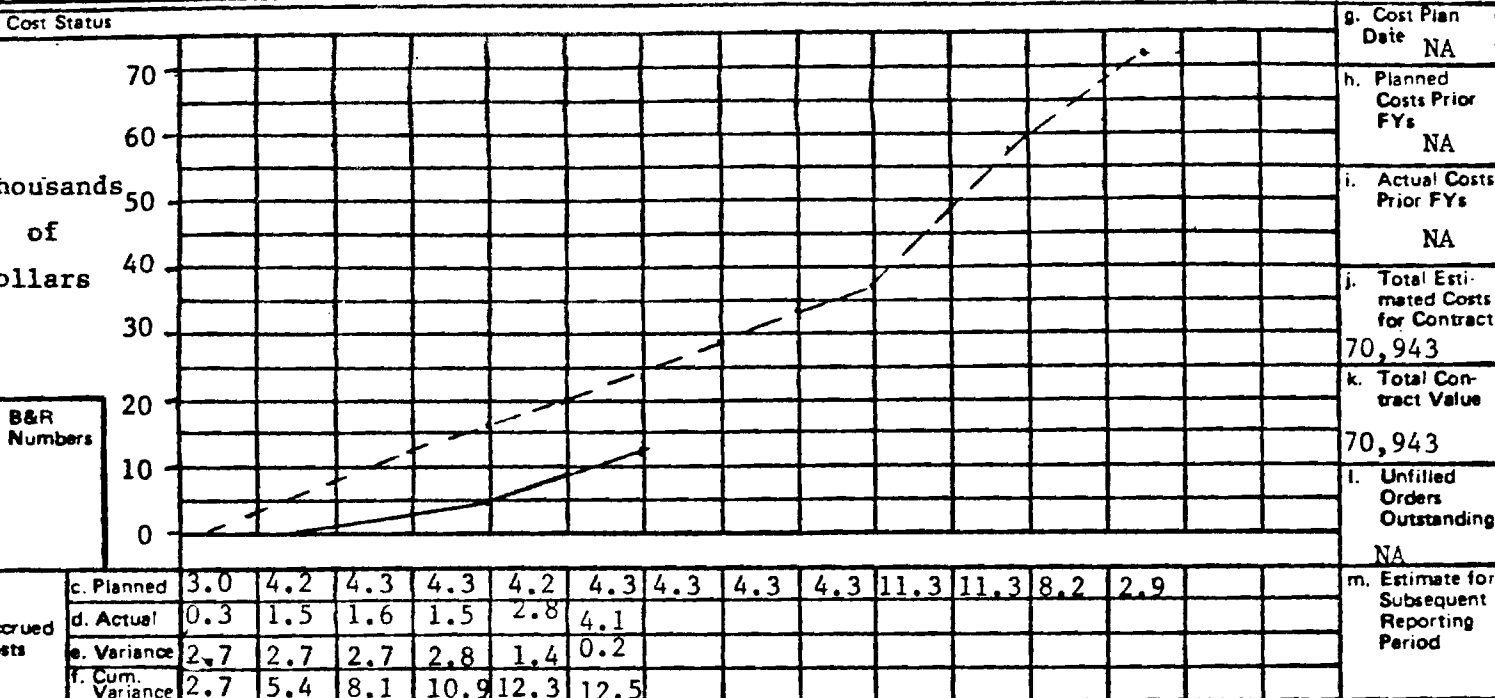
Bids are now being received for the equipment that is needed during the second year of the program. Construction of the ANL design high-speed centrifugal contactor bank has begun. Overall the program is largely on schedule.

1. Contract Identification	2. Reporting Period	3. Contract Number
Fuel Grade Ethanol Recovery by Solvent Extraction	2/1/81 through 2/28/81	XK-0-9082-1

4. Contractor (Name and Address):	
Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, GA 30332	5. Contract Start Date 8/15/80
	6. Contract Completion Date 8/15/81

Months	S	O	N	D	J	F	M	A	M	J	J	A	S				8. FY81

Cost Status

Thousands of Dollars (y-axis: 0, 10, 20, 30, 40, 50, 60, 70)

B&R Numbers

		S	O	N	D	J	F	M	A	M	J	J	A	S			
Accrued Costs	c. Planned	3.0	4.2	4.3	4.3	4.2	4.3	4.3	4.3	4.3	11.3	11.3	8.2	2.9			
	d. Actual	0.3	1.5	1.6	1.5	2.8	4.1										
	e. Variance	2.7	2.7	2.7	2.8	1.4	0.2										
	f. Cum. Variance	2.7	5.4	8.1	10.9	12.3	12.5										

9.	
g. Cost Plan Date	NA
h. Planned Costs Prior FYs	NA
i. Actual Costs Prior FYs	NA
j. Total Estimated Costs for Contract	70,943
k. Total Contract Value	70,943
l. Unfilled Orders Outstanding	NA
m. Estimate for Subsequent Reporting Period	

Manpower Status (Direct Labor)

Labor	b. Planned																
	c. Actual																
	d. Variance																

e. Manpower Plan Date	
f. Planned Manpower Prior FYs	
g. Actual Manpower Prior FYs	
h. Total Estimated Manpower for Contract	
i. Total Contract Manpower	

Major Milestone Status

Phosphate Synthesis	
Alternates Synthesis	
Scoping Tests	
Batch Tests	
Equipment Set Up	
Continuous Tests	
Solvent Selection	

Remarks

Signature of Contractor's Project Manager and Date

14. Signature of Government Technical Representative and Date

GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

SCHOOL OF
CHEMICAL ENGINEERING

April 10, 1981

MEMORANDUM

TO: Distribution

FROM: D. W. Tedder

RE: Fuel-Grade   Ethanol Recovery by Solvent Extraction: Progress and
         Contract Management Summary Reports - SERI No. XK-0-9082-1, GTRI
         Nos. E-19-628 and G-33-674.

     Please find the attached reports for this time period. Thank you
for your time and consideration.

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Fuel-Grade Ethanol Recovery by Solvent Extraction:

March 1981 Contract Management

Summary Report

(SERI No. XK-0-9082-1)

D. W. Tedder and C. L. Liotta*

Georgia Tech Process Design Institute

School of Chemical Engineering

Georgia Institute of Technology

Atlanta, Georgia 30332

During this period the semiannual technical progress report was pre-
pared and submitted to SERI. The results were highly favorable and sug-
gest that 60 vol % tridecanol (TDOH) in n-dodecane (NDD) can be used to
recover an ethanol product that is about 93.7 wt % ethanol. The required
organic-to-aqueous flow ratio is about three-to-one which is substantially
less than the ten-to-one ratio that was assumed in the initial research
proposal for this project. In addition, the mutual solubility curves
for kerosene, dodecane and a mixture of 30 vol % 2-ethyl-1,3-hexane diol(EHD)
in kerosene were measured and their tie lines calculated. The system
30 % EHD in kerosene is drier than the 60% TDOH/NDD system, but ethanol
extraction in the former case results in the formation of a third phase.

*School of Chemistry, Georgia Institute of Technology

Considerable progress was made this quarter in identifying chemical systems that have both favorable ethanol distribution coefficients when the organic phase is equilibrated with aqueous mixtures containing low ethanol (i.e. less than 5%) concentrations and that appear capable of producing an ethanol product which is above the azeotrope (i.e. greater than 96% ethanol). Although an improved system may be readily synthesized from commercially available substances (e.g by reductive coupling of 2-ethyl hexanol), it appears that trideanol mixed isomer systems or dodecyl alcohol, perhaps, can be blended with n-dodecane to achieve a solvent mixture with suitable physical properties. An attractive system will probably contain from 30 to 60 vol % of these alcohols in the diluent. We will titrate these systems next month and, hopefully, we will be in a favorable position to begin batch countercurrent extractions with separatory funnels before May. Since all of these materials are inexpensive, commercially available, and exhibit low aqueous phase solubilities, the costs associated with solvent make-up are expected to be low.

Since most of the supply money in the E-19-628 account is depleted, some of the personnel services will be converted into supply funds in the near future.

Construction on the bank of high-speed centrifugal contactors is continuing and we have sent out a purchase order for a bank of SRL type mini-mixer-settlers to the Gentry Instruments, Co. in Aiken, S.C. Fabrication time is estimated to be six months. We are also purchasing pumps that will be required to operate the process continuously from FMI and are making plans to begin construction of a suitable stripping apparatus to connect to the solvent extraction cascade.

CONTRACT MANAGEMENT SUMMARY REPORT

FORM DOE 536
(1/78)

FORM APPROVED
OMB NO. 38R—0190

1. Contract Identification	2. Reporting Period	3. Contract Number
Fuel Grade Ethanol Recovery by Solvent Extraction	3/1/81 through 3/31/81	XK-0-9082-1

4. Contractor (Name and Address)	
Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, GA 30332	5. Contract Start Date 8/15/80
	6. Contract Completion Date 8/15/81

7. Months	S	O	N	D	J	F	M	A	M	J	J	A	S			8. FY 81

9. Cost Status

a.

Thousands of Dollars

70 — 60 — 50 — 40 — 30 — 20 — 10 — 0

b. B&R Numbers

		S	O	N	D	J	F	M	A	M	J	J	A	S			
Accrued Costs	c. Planned	3.0	4.2	4.3	4.3	4.2	4.3	4.3	4.3	4.3	11.3	11.3	8.2	2.9			
	d. Actual	0.3	1.5	1.6	1.5	2.8	4.1	4.9									
	e. Variance	2.7	2.7	2.7	2.8	1.4	0.2	(0.6)									
	f. Cum. Variance	2.7	5.4	8.1	10.9	12.3	12.5	11.9									

g. Cost Plan Date	NA
h. Planned Costs Prior FYs	NA
i. Actual Costs Prior FYs	NA
j. Total Estimated Costs for Contract	70,943
k. Total Contract Value	70,943
l. Unfilled Orders Outstanding	NA
m. Estimate for Subsequent Reporting Period	

10. Manpower Status (Direct Labor)

a.

Man-power	b. Planned																
	c. Actual																
	d. Variance																

e. Manpower Plan Date

f. Planned Manpower Prior FYs

g. Actual Manpower Prior FYs

h. Total Estimated Manpower for Contract

i. Total Contract Manpower

11. Major Milestone Status

- Phosphate Synthesis
- Alternates Synthesis
- Scoping Tests
- Batch Tests
- Equipment Set Up
- Continuous Tests
- Solvent Selection

12. Remarks

13. Signature of Contractor's Project Manager and Date	14. Signature of Government Technical Representative and Date
4/10/81	

SCHOOL OF
CHEMICAL ENGINEERING

June 8, 1981

MEMORANDUM

TO: Distribution

FROM: D. W. Tedder   RE: April Contract Report

RE: Fuel-Grade Ethanol Recovery by Solvent Extraction: Progress and
        Contract Management Summary Reports - SERI No. XK-0-9082-1, GTRI
        Nos. E-19-628 and G-33-674.

    Please find the attached reports for this time period. Thank you
for your time and consideration. Please accept my apologies for the
delay.

Distribution: J. A. Bertrand (1 copy)
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Fuel-Grade Ethanol Recovery by Solvent Extraction:

April 1981 Contract Management

Summary Report

(SERI No. XK-0-9082-1)

D. W. Tedder and C. L. Liotta*

Georgia Tech Process Design Institute

School of Chemical Engineering

Georgia Institute of Technology

Atlanta, Georgia   30332

At the beginning of this period, Dr. Tedder attended the SERI contractors' meeting that was held in Denver, Colorado and presented the program results which were available at that time. The experimental evaluations of ethanol recovery solvent systems continue to appear favorable. At the meeting, results were presented for pure kerosene, n-dodecane, and two modified systems: 30 vol % 2-ethyl-1,3-hexane diol in kerosene and 60 vol % tridecanol in n-dodecane. Subsequently, tests have been carried out to further optimize the vol percentage of modifier that should be added to a diluent in order to obtain the correct physical properties. In general, the addition of increased volume percentages of an alcohol modifier increases the ethanol distribution coefficients, especially at low ethanol concentrations in the equilibrated aqueous phase, but it also decreases the solvent selectivity and, therefore, the ultimate ability of the solvent to dry the ethanol product. These two factors are

*School of Chemistry, Georgia Institute of Technology

in competition with each other and must be assessed in an integrated fashion that considers both effects.

It has become apparent that n-dodecane is too expensive to use as a diluent in commercial recovery systems. Therefore, substitutes are being examined. An inexpensive refinery product, NORPAR-12, is available from Exxon, for example, and its cost is comparable to that of kerosene. Alternatively, Exxon also sells a higher molecular weight normal paraffinic fraction that is referred to as NORPAR-13. Several isoparaffinic fractions are also available from Exxon. Samples of these candidate diluents have been ordered and they will be tested as soon as they are received.
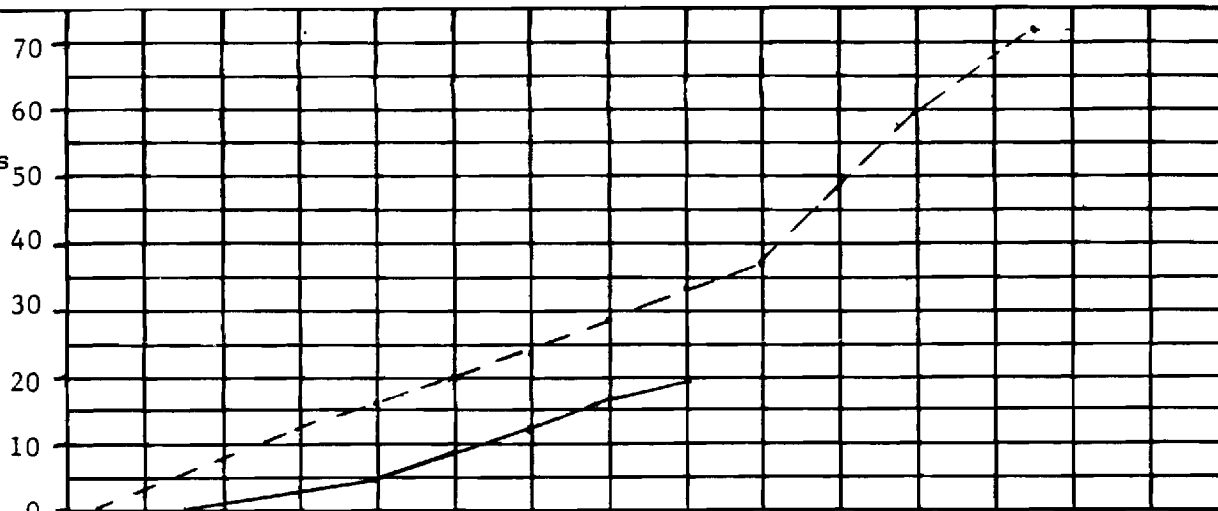
Another candidate extraction system consists of mixtures of dodecylbenzene and dodecylphenol. Both of these substances are available in bulk quantitites and are relatively inexpensive since they are used as chemical intermediates, primarily in detergents. Samples have been requested from Chevron and Tennessee Eastman.
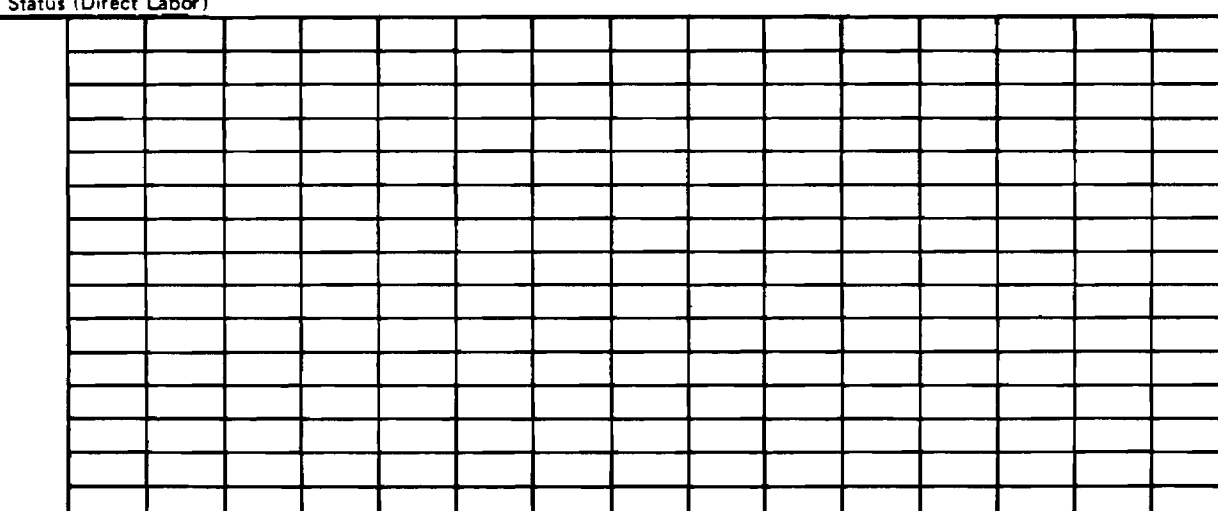
Conoco produces a waste byproduct stream that consists of mixed isomers of high molecular weight dienes. This material could be used as a starting formulation to produce several diols and, possibly, triols inexpensively. Samples have been ordered and will be converted to the appropriate alcohol for use as modifiers.
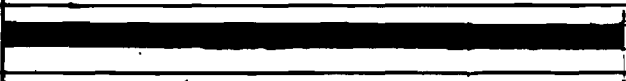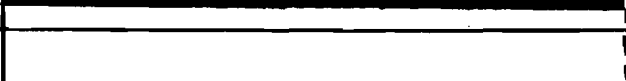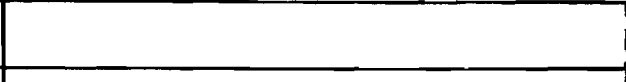
Progress continues in the construction of a bank of the Argonne type high-speed centrifugal contactors. Work is now about 60 % completed. We expect to begin operation of one or more continuous systems by the early fall.

U.S. DEPARTMENT OF ENERGY

FORM DOE 536
1/78)

CONTRACT MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 38R—0190

1. Contract Identification	2. Reporting Period	3. Contract Number
Fuel Grade Ethanol Recovery by Solvent Extraction	4/1/81 through 4/30/81	XK-0-9082-1

4. Contractor (Name and Address)

Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, GA 30332

5. Contract Start Date
8/15/80

6. Contract Completion Date
8/15/81

7. Months	S	O	N	D	J	F	M	A	M	J	J	A	S			8. FY81

9. Cost Status

g. Cost Plan Date NA

h. Planned Costs Prior FYs NA

i. Actual Costs Prior FYs NA

j. Total Estimated Costs for Contract 70,943

k. Total Contract Value 70,943

l. Unfilled Orders Outstanding NA

m. Estimate for Subsequent Reporting Period

Accrued Costs		S	O	N	D	J	F	M	A	M	J	J	A	S		
	c. Planned	3.0	4.2	4.3	4.3	4.2	4.3	4.3	4.3	4.3	11.3	11.3	8.2	2.9		
	d. Actual	0.3	1.5	1.6	1.5	2.8	4.1	4.9	3.2							
	e. Variance	2.7	2.7	2.7	2.8	1.4	0.2	(0.6)	1.1							
	f. Cum. Variance	2.7	5.4	8.1	10.9	12.3	12.5	11.9	13.0							

10. Manpower Status (Direct Labor)

e. Manpower Plan Date

f. Planned Manpower Prior FYs

g. Actual Manpower Prior FYs

h. Total Estimated Manpower for Contract

i. Total Contract Manpower

Manpower	b. Planned															
	c. Actual															
	d. Variance															

11. Major Milestone Status

a. Phosphate Synthesis	
b. Alternates Synthesis	
c. Scoping Tests	
d. Batch Tests	
e. Equipment Set Up	
f. Continuous Tests	
g. Solvent Selection	
h.	
i.	

12. Remarks

13. Signature of Contractor's Project Manager and Date

14. Signature of Government Technical Representative and Date

SCHOOL OF
CHEMICAL ENGINEERING

June 8, 1981

MEMORANDUM

TO: Distribution

FROM: D. W. Tedder   RE: May Contract Report

RE: Fuel-Grade Ethanol Recovery by Solvent Extraction: Progress and
         Contract Management Summary Reports - SERI No. XK-O-9082-1, GTRI
         Nos. E-19-628 and G-33-674.

     Please find the attached reports for this time period. Thank you
for your time and consideration.

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Fuel-Grade Ethanol Recovery by Solvent Extraction:

May 1981   Contract Management

Summary Report

(SERI No. XK-0-9082-1)

D. W. Tedder and C. L. Liotta*

Georgia Tech Process Design Institute

School of Chemical Engineering

Georgia Institute of Technology

Atlanta, Georgia   30332

During this period, a proposal for renewal was completed and
submitted to SERI. The design calculations for this case were based
on a system consisting of two extraction cycles. In the first cycle,
the ethanol and water are coextracted to yield an ethanol product that
is about 90 wt % ethanol. In the second cycle, the cascade is operated
so that at least a 98 wt % ethanol product is produced, but the raffinate
becomes a recycle stream to the first cascade. This strategy appears
more effective in reducing costs and energy consumption than the alternatives
which were considered, including: (1) high solvent loading in the first
cycle to dry the product, (2) azeotropic and extractive distillation using
conventional methods, and (3) vacuum distillation of the 90 wt % product
to achieve a "fuel-grade" product.

*School of Chemistry, Georgia Institute of Technology

The original research proposal to SERI indicated that ethanol might be recovered from dilute fermentation liquors using solvent extraction and expending no more than about 10 % of the heating value of the ethanol product. The renewal proposal arrived at about the same level of energy consumption, but concludes that two extraction cycles are needed. The first cycle operates as a recovery system which exhaustively extracts the ethanol away from the bulk of the water. The second cycle operates as a drying cycle to upgrade the ethanol product to a fuel-grade (i.e. 98 wt % or better) level. This strategy does further increase the required capital investment, but the energy consumption remains low because the reflux is only about 10 to 20 % of the product rate (rather than 500 to 600 % as in distillation) and because the required stripping conditions are less severe than were assumed in the original proposal. That is, the original research proposal assumed "worst case" conditions for stripping and refrigeration; subsequent experimental stripping tests have been favorable and suggest that adequate conditions exist at warmer temperatures and higher pressures than were originally assumed. Therefore, the adverse impact of the second cycle has been cancelled out by the favorable results of the stripping tests.
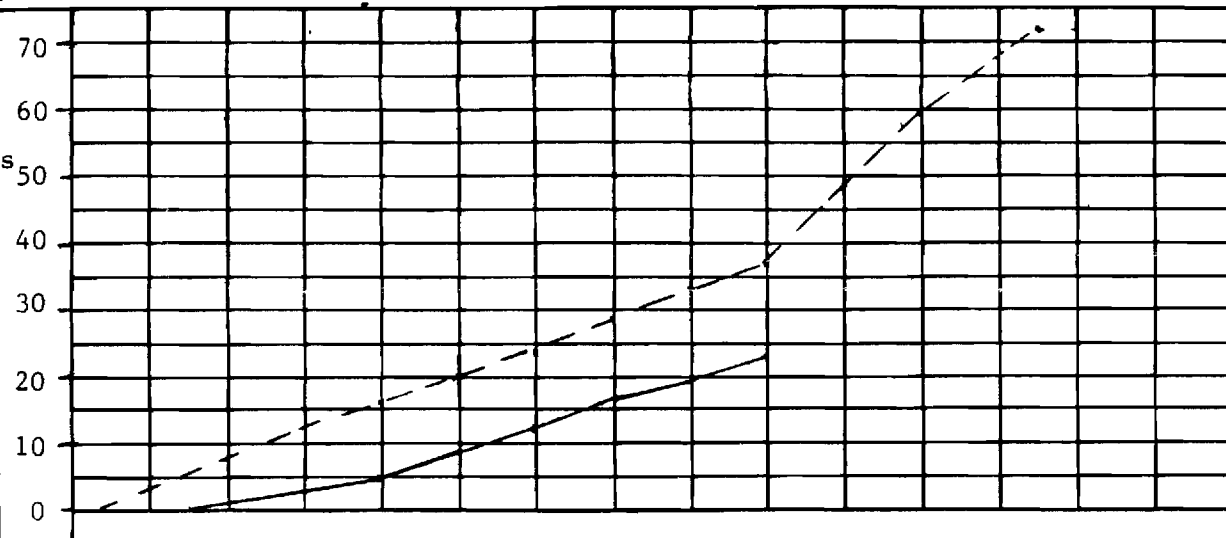
A two cycle concept for recovery also effects the strategy for solvent selection. Previously, efforts have been oriented toward achieving both high distribution coefficients and adequate selectivity in a single solvent. However, the two cycle concept of recovery permits the use of a high recovery solvent in the first solvent cycle and a high selectivity solvent in the second cycle. In all probability, the first cycle would consist of a diluent plus a modifier while the second cycle would consist simply of the same diluent without the modifier. Thus, only two solvent species are needed, rather than three, but differences exist in the compositions of the two solvents.
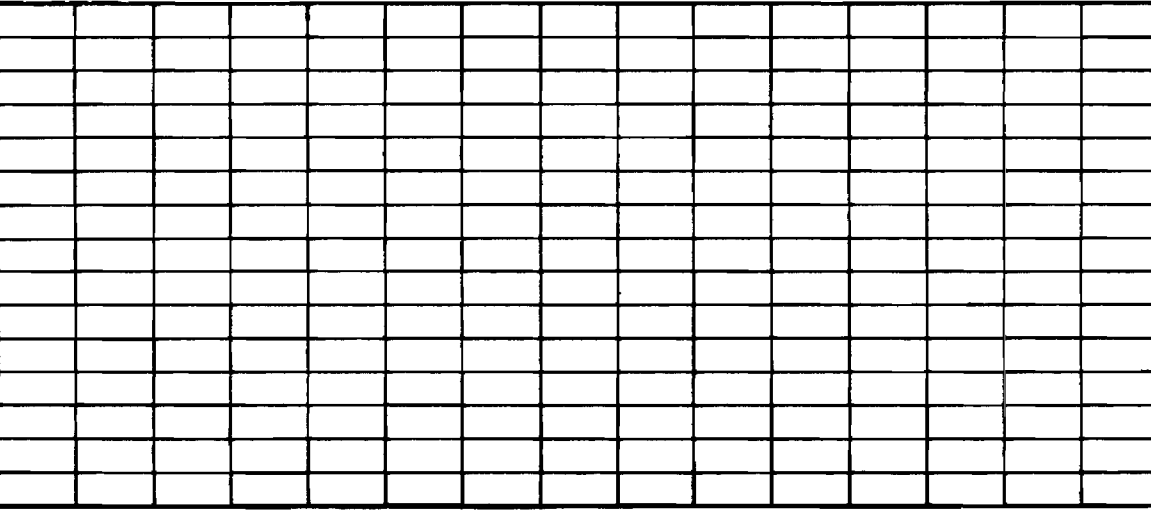
Consistent with the proposed flowsheet changes, plans are being made to investigate the use of several diluent and modifier systems, but with varied levels of modifier. In particular, we plan to examine systems containing 10 vol %, 30 vol % and 50 vol % modifier in a diluent for several different combinations. Diluents include: kerosene, NORPAR-12, ISOPAR-G, dodecylbenzene, and n-dodecane. Modifiers include: tridecanol, isooctanol, n-dodecyl alcohol, and several diols.
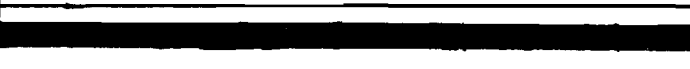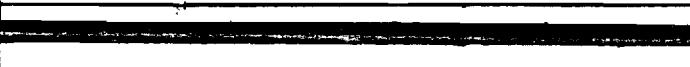
CONTRACT MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 38R—0190

1. Contract Identification	2. Reporting Period	3. Contract Number
Fuel Grade Ethanol Recovery by Solvent Extraction	5/1/81 through 5/31/81	XK-0-9082-1

4. Contractor (Name and Address)
Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, GA 30332

5. Contract Start Date 8/15/80

6. Contract Completion Date 8/15/81

7. Months	S	O	N	D	J	F	M	A	M	J	J	A	S			8. FY81

9. Cost Status

Thousands of Dollars (vertical axis: 0, 10, 20, 30, 40, 50, 60, 70)

g. Cost Plan Date NA

h. Planned Costs Prior FYs NA

i. Actual Costs Prior FYs NA

j. Total Estimated Costs for Contract 70,943

k. Total Contract Value 70,943

l. Unfilled Orders Outstanding NA

m. Estimate for Subsequent Reporting Period

b. B&R Numbers

Accrued Costs		S	O	N	D	J	F	M	A	M	J	J	A	S		
	c. Planned	3.0	4.2	4.3	4.3	4.2	4.3	4.3	4.3	4.3	11.3	11.3	8.2	2.9		
	d. Actual	0.3	1.5	1.6	1.5	2.8	4.1	4.9	3.2	3.2						
	e. Variance	2.7	2.7	2.7	2.8	1.4	0.2	(0.6)	1.1	1.1						
	f. Cum. Variance	2.7	5.4	8.1	10.9	12.3	12.5	11.9	13.0	14.1						

10. Manpower Status (Direct Labor)

e. Manpower Plan Date

f. Planned Manpower Prior FYs

g. Actual Manpower Prior FYs

h. Total Estimated Manpower for Contract

i. Total Contract Manpower

Manpower																
	b. Planned															
	c. Actual															
	d. Variance															

11. Major Milestone Status

a. Phosphate Synthesis
b. Alternates Synthesis
c. Scoping Tests
d. Batch Tests
e. Equipment Set Up
f. Continuous Tests
g. Solvent Selection
h.
i.

12. Remarks

13. Signature of Contractor's Project Manager and Date 6/8/81

14. Signature of Government Technical Representative and Date

July 10, 1981

-MEMORANDUM

TO: Distribution

FROM: D. W. Tedder

RE: Fuel-Grade Ethanol Recovery by Solvent Extraction: Progress and
         Contract Management Summary Reports - SERI No. XK-0-9082-1, GTRI
         Nos. E-19-628 and G-33-674.

     Please find the attached reports for this time period. Thank you
for your time and consideration.

Distribution: J. A. Bertrand (1 copy)
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Fuel-Grade Ethanol Recovery by Solvent Extraction:

June 1981 Contract Management

Summary Report

(SERI No. XK-0-9082-1)

D. W. Tedder and C. L. Liotta*

Georgia Tech Process Design Institute

School of Chemical Engineering

Georgia Institute of Technology

Atlanta, Georgia   30332

During this period, several additional solvent extraction systems
were titrated and considered as extractants. These solvents include
an initial evaluation of the potential diluents, NORPAR 12 and NORPAR 13,
which may be used as substitutes for n-dodecane. Also, the refinery
products, ISOPAR G and ISOPAR L, were examined using an analytical determination
of the distribution coefficients. These determinations were made using
the new GC and Hewlette Packard integrator. The apparent distribution
coefficients for ethanol are close together (about 0.4) and the water
distribution coefficient was too   small to be measured accurately.

*School of Chemistry, Georgia Institute of Technology

Based upon the most recent analysis of the solvent extraction recovery costs, it has become apparent that alternative diluents to n-dodecane must be found in order for the recovery to be economically attractive. Consequently, several refinery products were ordered from Exxon which are comparable in cost to kerosene. They arrived late in the month and we have completed an initial evaluation of the mutual solubility curves. The results look encouraging and it appears possible to achieve a 99 wt % ethanol product using pure NORPAR 12. We have not completed our analysis of the ISOPAR diluents, but it appears likely that these materials are all suitable for this application.

Several other mixtures were titrated this month. These include: 10 % dodecyl alcohol in n-dodecane, 10 % dodecylphenol in n-dodecane, 10 % dodecylphenol in kerosene, and 10 % tridecyl alcohol in kerosene. In addition, the systems 20 % isodecyl alcohol in n-dodecane, 30 % dodecyl alcohol in kerosene, 30 % dodecyl phenol in kerosene, 40 % dedecyl alcohol in n-dodecane, and 100 % dodecyl alcohol were titrated. Our analysis is not yet complete, but kerosene does not appear as attractive as the Exxon refinery products.

During this month we received the new GC and LC equipment. The GC is now operational and we have begun making determinations. It is equipped with a 3390A HP recording integrator that stores the peaks electronically and prints out the resulting area percentages associated with each of the peaks. It appears to be highly reproducible and the plots of percentage ethanol area versus the aqueous ethanol weight percentage is nearly linear. Consequently, a batch equilibration was attempted in which approximately equal amounts of tridecyl alcohol were equilibrated with an aqueous phase and one of four different diluents: NORPAR 12, NORPAR 13, ISOGAR G or ISOPAR L. The equilibrated aqueous phases were analyzed with the GC and the ethanol distribution coefficients were measured. The water distribution coefficients, however, were too small to be measured using this method and we will continue to evaluate alternative approaches. The results are summarized below as tables 1 and 2.

Table 1. Ethanol extraction data

	D_{ETOH}	$\dfrac{ETOH}{TDOH}$[a]
NORPAR 12	.366	.592
NORPAR 13	.349	.606

[a] Grams of ethanol divided by the grams of tridecyl alcohol

Table 2. Ethanol extraction data

	D_{ETOH}	$\dfrac{ETOH}{TDOH}$[a]
ISOPAR G	.404	.599
ISOPAR L	.384	.639

[a] Grams of ethanol divided by the grams of tridecyl alcohol

Based on the data in Tables 1 and 2, it appears that the ISOPAR diluents are slightly better than the NORPAR diluents. In these experiments it was not possible to measure the water distribution coefficient which is apparently less than the error in the experiment. However, we can conclude that ethanol does extract into these mixtures while the water is extracted only slightly, if at all.
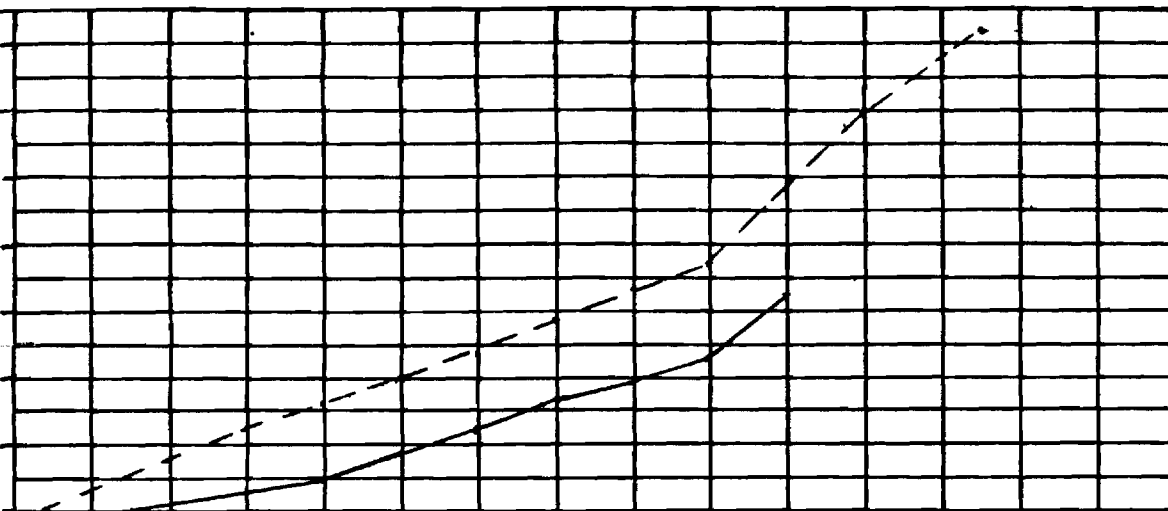
Comparison of this data with the distribution coefficients that are predicted from the mutual solubility curve titrations show reasonable agreement. Although the analytical distribution coefficients for ethanol shown above are slightly less than predicted from the solubility curves, these differences are probably due to the fact that the samples were only equilibrated for one minute with moderate shaking. That is, the samples were probably not at equilibrium.
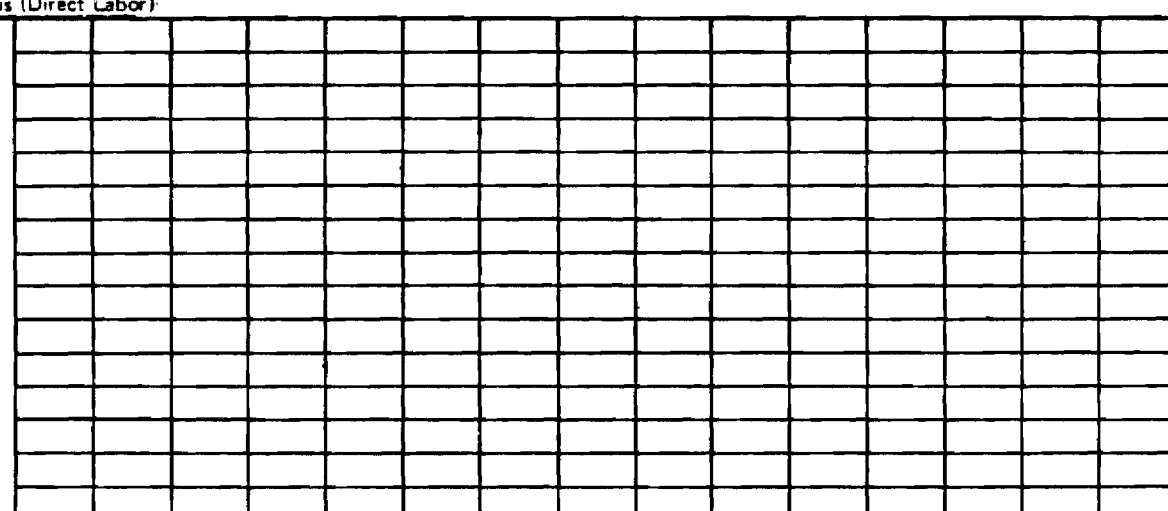
Work on the high-speed centrifugal contactors continues on schedule. This unit will probably be operational by the end of the summer.

ORM DOE 536
(/78)

CONTRACT MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 38R−0190

1. Contract Identification	2. Reporting Period	3. Contract Number
Fuel Grade Ethanol Recovery by Solvent Extraction	6/1/81 through 6/30/81	XK-0-9082-1

4. Contractor (Name and Address)	
Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, GA 30332	5. Contract Start Date 8/15/80
	6. Contract Completion Date 8/15/81

7. Months	S	O	N	D	J	F	M	A	M	J	J	A	S			8. FY81

9. Cost Status

Thousands of Dollars

70
60
50
40
30
20
10
0

b. B&R Numbers

g. Cost Plan Date NA

h. Planned Costs Prior FYs NA

i. Actual Costs Prior FYs NA

j. Total Estimated Costs for Contract 70,943

k. Total Contract Value 70,943

l. Unfilled Orders Outstanding NA

Accrued Costs		S	O	N	D	J	F	M	A	M	J	J	A	S		
	c. Planned	3.0	4.2	4.3	4.3	4.2	4.3	4.3	4.3	4.3	11.3	11.3	8.2	2.9		
	d. Actual	0.3	1.5	1.6	1.5	2.8	4.1	4.9	3.2	3.2	9.5					
	e. Variance	2.7	2.7	2.7	2.8	1.4	0.2	(0.6)	1.1	1.1	1.8					
	f. Cum. Variance	2.7	5.4	8.1	10.9	12.3	12.5	11.9	13.0	14.1	15.9					

m. Estimate for Subsequent Reporting Period

10. Manpower Status (Direct Labor)

a.

Man-power	b. Planned															
	c. Actual															
	d. Variance															

e. Manpower Plan Date

f. Planned Manpower Prior FYs

g. Actual Manpower Prior FYs

h. Total Estimated Manpower for Contract

i. Total Contract Manpower

11. Major Milestone Status

| a. Phosphate Synthesis |
| b. Alternates Synthesis |
| c. Scoping Tests |
| d. Batch Tests |
| e. Equipment Set Up |
| f. Continuous Tests |
| g. Solvent Selection |
| h. |
| i. |

12. Remarks

13. Signature of Contractor's Project Manager and Date	14. Signature of Government Technical Representative and Date

August 10, 1981

MEMORANDUM

TO: Distribution

FROM: D. W. Tedder

RE: Fuel-Grade Ethanol Recovery by Solvent Extraction: Progress and
        Contract Management Summary Reports - SERI No. XK-0-9082-1, GTRI
        Nos. E-19-628 and G-33-674.

     Please find the attached reports for this time period. Thank you
for your time and consideration.

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Fuel-Grade Ethanol Recovery by Solvent Extraction:

July 1981 Contract Management

Summary Report

(SERI No. XK-0-9082-1)

D. W. Tedder and C. L. Liotta*

Georgia Tech Process Design Institute

School of Chemical Engineering

Georgia Institute of Technology

Atlanta, Georgia   30332

The evaluation of alternative solvent extraction systems continued during this period. Since we have received the new GC equipment and peak integrator, we have begun to reevaluate systems that were studied earlier in the program as well as assess new solvents. Several phosphate systems have been reevaluated using our new, more accurate proceedures. These systems include 30 % TBP in dodecane and in NORPAR 12. We are also completing an evaluation of di-2-ethylhexyl phosphoric acid in NORPAR 12 and tricresyl phosphate in NORPAR 12. The conclusions for these mixtures are not expected to change significantly, although the estimated distribution coefficients and separation factors are more accurate.

The refinery products, such as NORPAR 12, NORPAR 13, ISOPAR G and ISOPAR L all appear roughly equivalent for this application to n-dodecane; however, they are much less expensive. Exxon is unwilling to sell NORPAR 12 in batches smaller than 9000 gal (at $1.82/gal FOB), but they are willing to give away five gallon samples. We received one such sample at the end of the month and are using it as a stand in for n-dodecane which is not available.

*School of Chemistry, Georgia Institute of Technology

We also completed an evaluation of 2-ethyhexanol as an extractant. The results indicate that this system has an ethanol distribution coefficient of about unity, but the separation factors are too low. It could be used, however, to produce about an 80 wt % ethanol product. On the other hand, if 2-ethylhexanol is mixed one-to-one with tridecyl alcohol, then the distribution coefficient for ethanol is about 0.8 and the separation factor is over 200. This system might be capable of producing a 98 wt % ethanol product at 10 wt % loading in a single cycle, but it has phase disengagement problems. In order to improve the phase disengagement, we are examining mixtures such as 50 vol % NORPAR 12, 25 vol % 2-ethylhexanol and 25 vol % decyl alchol. We are optimistic that a blend can be found which will permit the recovery of fuel-grade ethanol in a single extraction and stripping cycle, rather than in two cycles.

During the past year, the program has underspent its budget. This situation is due to the fact that a chemical engineering graduate student was not available during the first quarter and a chemistry graduate student was not available until the summer quarter of this year. Since then, however, we have been successful in obtaining several new chemical engineering students to work on the program as well as a chemistry student. In addition, 28 new graduate students will begin work in chemical engineering and it is probable that at least one new student will be available by the middle of the fall quarter to work on the research effort.

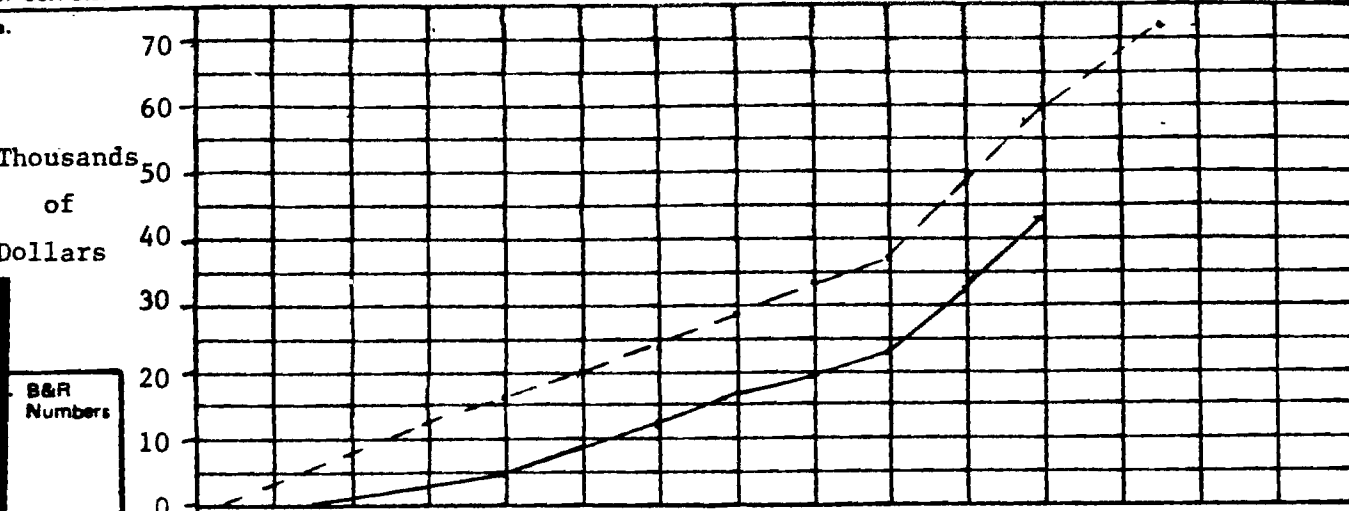Students now being funded by the research project are:

Kul B. Garg, M.S. , Chemical Engineering
Wahid Tawfik, M.S., Chemical Engineering
Lucia Krasnowski, M.S., Chemical Engineering
Charles Ray, M.S., Chemistry

We project, therefore, that the project will be only slightly under budget by the end of the fiscal year (about $7000) and that a slight over expenditure may occur during the second year of the program. In this event, the state of Georgia will participate in cost sharing with SERI to cover any cost overruns.

FORM DOE 536
(1/78)

CONTRACT MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 38R–0190

1. Contract Identification	2. Reporting Period	3. Contract Number
Fuel Grade Ethanol Recovery by Solvent Extraction	8/15/80 through 7/31/81	XK-0-9082-1

4. Contractor (Name and Address)

Georgia Tech Research Institute, Georgia Institute of Technology,
Atlanta, GA 30332

5. Contract Start Date 8/15/80

6. Contract Completion Date 8/15/81

7. Months	S	O	N	D	J	F	M	A	M	J	J	A	S			8. FY 81

9. Cost Status

Thousands of Dollars — chart (0 to 70)

B&R Numbers

g. Cost Plan Date NA

h. Planned Costs Prior FYs NA

i. Actual Costs Prior FYs NA

j. Total Estimated Costs for Contract 70,943

k. Total Contract Value 70,943

l. Unfilled Orders Outstanding NA

Accrued Costs	S	O	N	D	J	F	M	A	M	J	J	A	S
c. Planned	3.0	4.2	4.3	4.3	4.2	4.3	4.3	4.3	4.3	11.3	11.3	8.2	2.9
d. Actual	0.3	1.5	1.6	1.5	2.8	4.1	4.9	3.2	3.2	9.5	10.6		
e. Variance	2.7	2.7	2.7	2.8	1.4	0.2	(0.6)	1.1	1.1	1.8	0.7		
f. Cum. Variance	2.7	5.4	8.1	10.9	12.3	12.5	11.9	13.0	14.1	15.9	16.6		

m. Estimate for Subsequent Reporting Period

10. Manpower Status (Direct Labor)

e. Manpower Plan Date

f. Planned Manpower Prior FYs

g. Actual Manpower Prior FYs

h. Total Estimated Manpower for Contract

i. Total Contract Manpower

Manpower														
b. Planned														
c. Actual														
d. Variance														

Major Milestone Status

Phosphate Synthesis		
Alternates Synthesis		
Scoping Tests		
Batch Tests		
Equipment Set Up		
Continuous Tests		
Solvent Selection		

Remarks

13. Signature of Contractor's Project Manager and Date

14. Signature of Government Technical Representative and Date

FUEL-GRADE ETHANOL RECOVERY BY SOLVENT EXTRACTION. TECHNICAL PROGRESS REPORT

For Period September 15, 1980 through February 28, 1981

D. W. Tedder
C. L. Liotta*
F. M. Williams
M. A. Spanbauer

GEORGIA TECH

PROGRESS DESIGN INSTITUTE

SCHOOL OF CHEMICAL ENGINEERING

ATLANTA, GA. 30332 U.S.A.

*School of Chemistry, Georgia Institute of Technology, Atlanta, GA. U.S.A.

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GLOSSARY

ETOH	=	Ethanol
2EHOH	=	2-ethylhexanol
NDD	=	n-dodecane
HDEHP	=	di(2-ethylhexyl) phosphoric acid
TDOH	=	tridecanol
UNFOH	=	Umbrex-N- fatty alcohol
DEHEHP	=	di(2-ethylhexyl) 2-ethylhexyl phosphonate
TBP	=	tri-n-butyl phosphate
DBBP	=	Dibutyl butyl phosphonate
TLA	=	trilaurylamine
TLAO	=	trilaurylamine oxide
2EHOOH	=	2-ethylhexanoic acid
3HPOH	=	3-heptanol
NBUAC	=	n-butyl acetate
DNEHP	=	dineopentyl-2-ethyl hexyl phosphonate
D_e	=	distribution coefficient for ethanol either as concentration or weight ratios
D_w	=	distribution coefficient for water either as concentration or weight ratios

Fuel-Grade Ethanol Recovery by Solvent Extraction:

Technical Progress Report for September 15, 1980 through February 28, 1981

D.W. Tedder, C.L. Liotta*, F.M. Williams and M.A. Spanbauer

Georgia Tech Industrial Separations Laboratory
School of Chemical Engineering
Georgia Institute of Technology
Atlanta GA.   30332

ABSTRACT

Results are presented for scoping tests, batch equilibration data, mutual solubility curves and conceptual design studies which were completed either during this time period or prior to the start of the program. It appears likely that an efficient and cost-effective recovery system can be developed, but additional equilibration studies are needed to ensure that the solvent will be capable of adequately drying the alcohol product. The solvent 60 vol % tridecanol in n-dodecan appears capable of yielding an product that contains about 94 wt % ethanol.

*School of Chemistry, Georgia Institute of Technology, Atlanta, Ga. U.S.A.

The goal of this program is the development of a cost-effective and energy-efficient solvent extraction process which can recover fuel-grade ethanol from dilute fermentation liquors (~10% ethanol) for its ultimate use in producing gasahol. Moreover, the resulting recovery costs for the solvent extraction process should be less than those for ethanol recovery by optimized distillation. Previous study at Georgia Tech (1-4) resulted in a concept involving continuous fermentation, solvent extraction, and a solvent stripping step that can be accomplished in one of several ways. The initial case study (1) indicated that recovery tests might be reduced by 40% compared to a vacuum fermentor and conventional fractionator combination (5) that produced the 95% azeotrope. The projected savings are greater, however, when the comparisons include the benzene drying step. Also, the initial case design basis assumed an organic-to-aqueous volumetric flow ratio of about ten-to-one which now appears overly conservative.

The Georgia Tech process is based upon the assumption that a solvent phase exists which consists of chemical species that are high-boilers, relative to ethanol, and that can be reasonably used to separate ethanol from water. Under these conditions, the resulting clarified extract can then be stripped of its ethanol by vacuum distillation, for example, with the solvent recycled to the extraction cascade. The ethanol vapor must then be condensed to yield the final product and a reflux stream which is also sent back to the solvent extraction cascade.

The recovery process may also be used with continuous fermentation. In this case, there is recycle between the fermentor and the solvent extraction cascade. In particular, the extraction cascade receives a clarified liquor from the fermentor and returns its raffinate to the fermentor feed. Since the raffinate is contaminated with solvent, the solvent cannot be highly toxic to the yeast. On the other hand, there are favorable synergisms between the fermentation and the extraction cascade with respect to at least three effects. First, since the raffinate is a feed to the fermentor rather than a waste, the optimal alcohol recovery levels

are reduced. This effect makes the recovery step more energy-efficient. Second, the solvent extraction cascade can be operated so that the optimal ethanol concentrations in the fermentor can be maintained. This effect makes the fermentor more efficient. Third, the solvent losses from the extraction process are reduced by the fermentor since the clarified liquor is nearly saturated with the solvent. This effect increases the size of the feasible solvent set and reduces solvent costs. Thus, the habitual recycle between these two process steps is envisioned to have favorable effects on the overall production system that neither subsystem has alone.

1. Experimental

Prior to September 1980, the experimental effort focused on the use of organophosphorous compounds. Subsequently, the study was broadened to other classes of chemical species. Here we report our preliminary scouting, batch equilibration, mutual solubility curves, and extractant synthesis results.

1.1 Scouting Tests

In order to rapidly evaluate alternatives, we have developed a simple procedure which we have dubbed a "scouting test". A few milliliters of the candidate extractant and the water-ethanol mixture(s) are placed in separate test tubes and their respective indices of refraction are measured. Then approximately equal volumes of the aqueous and organic phase are equilibrated in a test tube by vigorous shaking for about one minute. Subsequently, the test tube is placed in a beaker until the phases separate. If necessary, the sample may be centrifuged until a sharp interface is obtained. The observer then notes any apparent changes in the organic and aqueous volumes, the index of refraction for each phase, and any other conditions such as a haze in either phase. The approximate disengagement time is also noted if the separation occurs within a few minutes. These results are summarized in Table 1 together with the major conclusion for each test.

Table 1. Scoring Test Results and Conclusions

Test	Nominal[b] % ETOH	Systems[a] ORGANIC	Refractive Index Changes AQUEOUS	ORGANIC	Percentage Volume[c] Increase	Other Observations	Conclusions[d]
1	10	1+1-NDD+TLA	0	0	0	both phases clear, rapid disengagement	negligible phase transfer
2	10	1+1-NDD+HDEHP	+0.0019	-0.0015	+	both phases slightly hazy disengagement in about 5 min.	more water than ethanol extracted and/or the solvent is noticeably water soluble
3	10	TDOH	-0.0011	-0.0031	+		more ethanol than water extracted
4	70	TDOH	-0.0051	-0.0296	+60	centrifuged to form a hazy organic and clear aqueous phase	" " " " "
5	60	UNFOH	+0.0469	-0.026	+80	both phases hazy, disengaged in about 10 min.	more water than ethanol extracted and/or the solvent is noticeably water soluble
6	60	2EHOH	-0.0133	-0.0204	+	two clear phases	more ethanol than water extracted
7	60	DEHEHP	-0.0041	-0.0200	+	hazy aqueous, clear organic	" " " " "
8	60	1+1-TDOH+DEHEHP	-0.0025	-0.0241	0	hazy organic clear aqueous	" " " " "
9	60	1+1-2EHOH+DEHEHP	-0.004	-0.0130	0	hazy aqueous, clear organic	" " " " "
10	60	1+1-2EHOH+TLAO				formed three phases	inappropriate extractant
11	5	1-butanol	+0.0084	-0.0057			more water than ethanol extracted and/or the solvent is noticably water soluble
12	5	2EHOH	-0.0003	+0.0008			more ethanol than water extracted
13	60	2EHOH	-0.0093	-0.1224	+40	centrifuged to give two clear phases	" " " " "
14	60	2EHOH	-0.0118	-0.0231	+50	centrifuged to give clear organic and hazy aqueous phase	" " " " "
15	60	1+1-2EHOH+TDOH	-0.0088	-0.0254	+50	centrifuged to give two slightly hazy phases	" " " " "
16	60	1-butyl acetate	-0.008	-0.0129	+65	centriguged to give two clear phases	" " " " "
17	60	amylacetate	-0.0067	-0.0125	+50	centrifuged to give two clear phases	" " " " "
18	60	EHOH	-0.009	-0.0268	+50	two clear phasees, rapid disengagement	" " " " "
19	60	HDEHP	-0.003	-0.027	+40	centrifuged to give clear phases	" " " " "
20	60	TBP	-0.007	-0.028	+50	centrifuged to give two clear phases	" " " " "
21	60	1+1-2EHOH+HDEHP	-0.0087	-0.0242	+50		" " " " "
22	60	1+1-TBP+HDEPH	-0.008	-0.0227	+60		" " " " "
23	60	2EHOH	-0.0062	-0.0016	+50		" " " " "
24	60	2EHOOH	+0.0482	-0.0184	+50		more water than ethanol extracted and/or the solvent is noticeably water soluble
25	60	1+1-2EHOH+2EHOOH	-0.0062	-0.0195	+50		more ethanol than water extracted
26	60	30% TBP in NDD					

[a] Approximately equal volumes were equilibrated.

[b] Approximate initial volume percentage of ethanol in water.

[c] Approximate organic volume increase (when positive) as a percentage of the initial organic volume.

[d] Based on batch equilibration measurements.

1.2   Batch Equilibration Tests

Several organophosphorous compounds were tested to determine their ability to selectively remove ethanol from dilute aqueous mixtures. In each case, equal volumes of a 1.1 molar (M) solution of extractant and diluent and aqueous ethanol-water mixture were placed in a separatory funnel. The extractants, chemicals interacting with the solute, were limited to organophosphorous compounds. The diluent, dodecane (NDD) was used to reduce the extractant viscosity and the organic phase density. The mixture in the separatory funnel was shaken for five minutes, then allowed to equilibrate for forty-five minutes. In every case except one, the mixtures formed two immiscible phases. However, when sixty volume per cent ethanol-water and TBP-NDD were equilibrated, a three phase mixture resulted.

After equilibration, the two phase systems were separated. The resulting aqueous was then analyzed by a density measurement and NMR spectrum to establish the equilibrium ethanol and water concentrations. The spectra were analyzed by integrating the -OH peak at 4.5ppm and that for the -CH_3 group at 1ppm. The ratio of the areas was then used to estimate concentrations.

The organic phase was then placed in a round-bottom flask with a stirring bar and stripped at room temperature and 1mm Hg, in the apparatus shown as Figure 1. The vacuum stripping for the mixture was continued 30 minutes beyond that time at which any bubbling in the solvent ceased to occur. After stripping, the residual solvent in the round-bottom flask was examined by a density measurement and another NMR spectrum.

Referring to Figure 1, the ethanol and water vapors which are stripped from the round-bottom flask migrate toward two condensers in series. The condensers consist of cold fingers that are submerged in liquid nitrogen. The second condenser, however, was not observed to have significant amounts of ethanol and water product, but simply served to protect the vacuum pump. After stripping the solvent

Figure 1

VACUUM STRIPPING APPARATUS
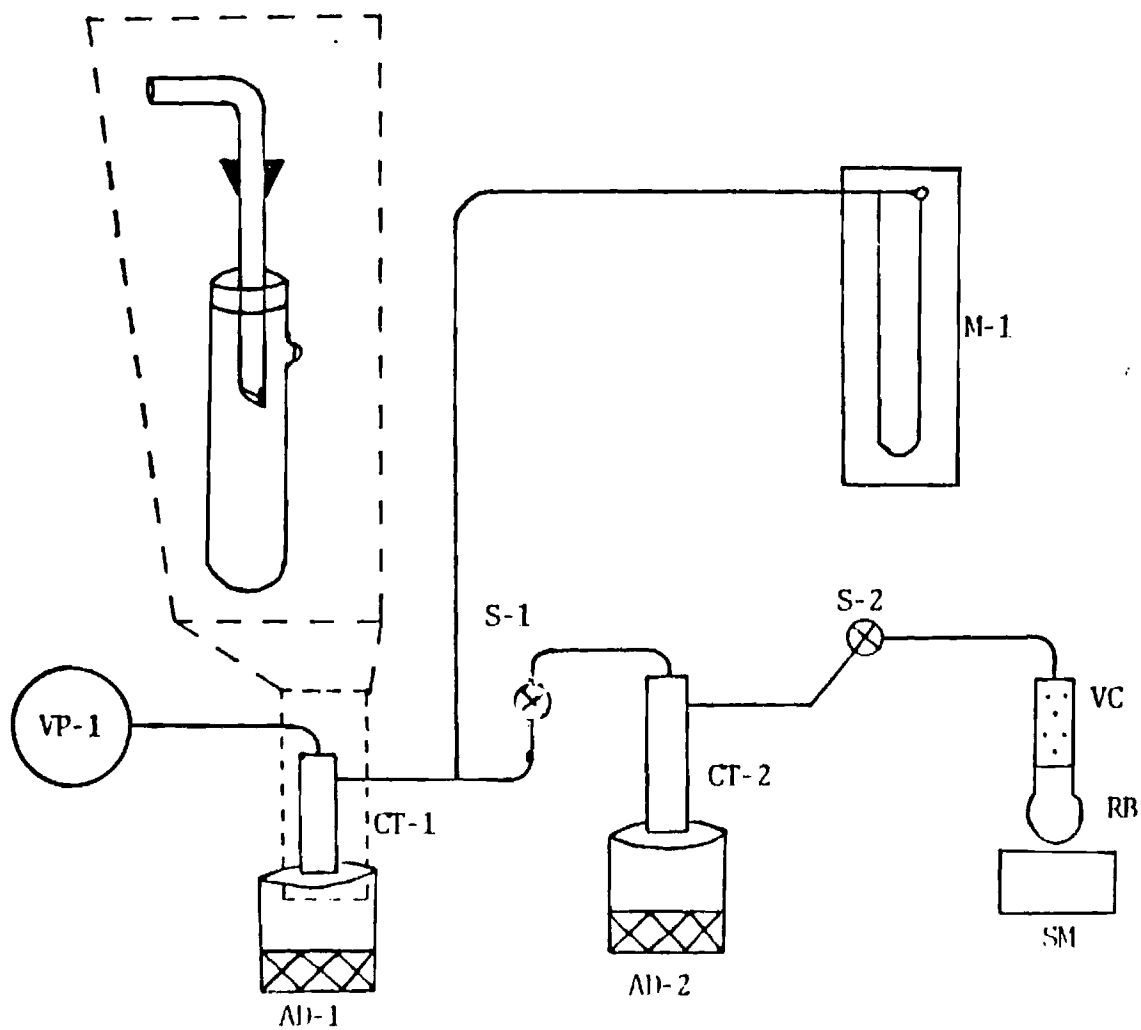
KEY

VP	VACUUM PUMP
CT	COLD TRAP
AD	ACETONE-DRY ICE BATH
SM	STIRRING MOTOR
RB	ROUND BOTTOM FLASK
VC	VIGOREAUX COLUMN
S	STOPCOCK
M	U-TUBE MONOMETER

7

for a period of time, the cold fingers were removed from the liquid nitrogen, allowed to come to room temperature, and sampled for a density measurement and a NMR spectrum.

Table 2 summarizes the solubilities of several different organophosphorous compounds that were of interest for this study. Figure 2 summarizes the distribution coefficients that were calculated for the TBP, DNEHP and DBBP extractants in NDD. These results are compared to the vapor/liquid equilibrium curve for the ethanol-water system in Figure 3.

TABLE 2. Solubility of Organophosphorous Compounds in n-dodecane.

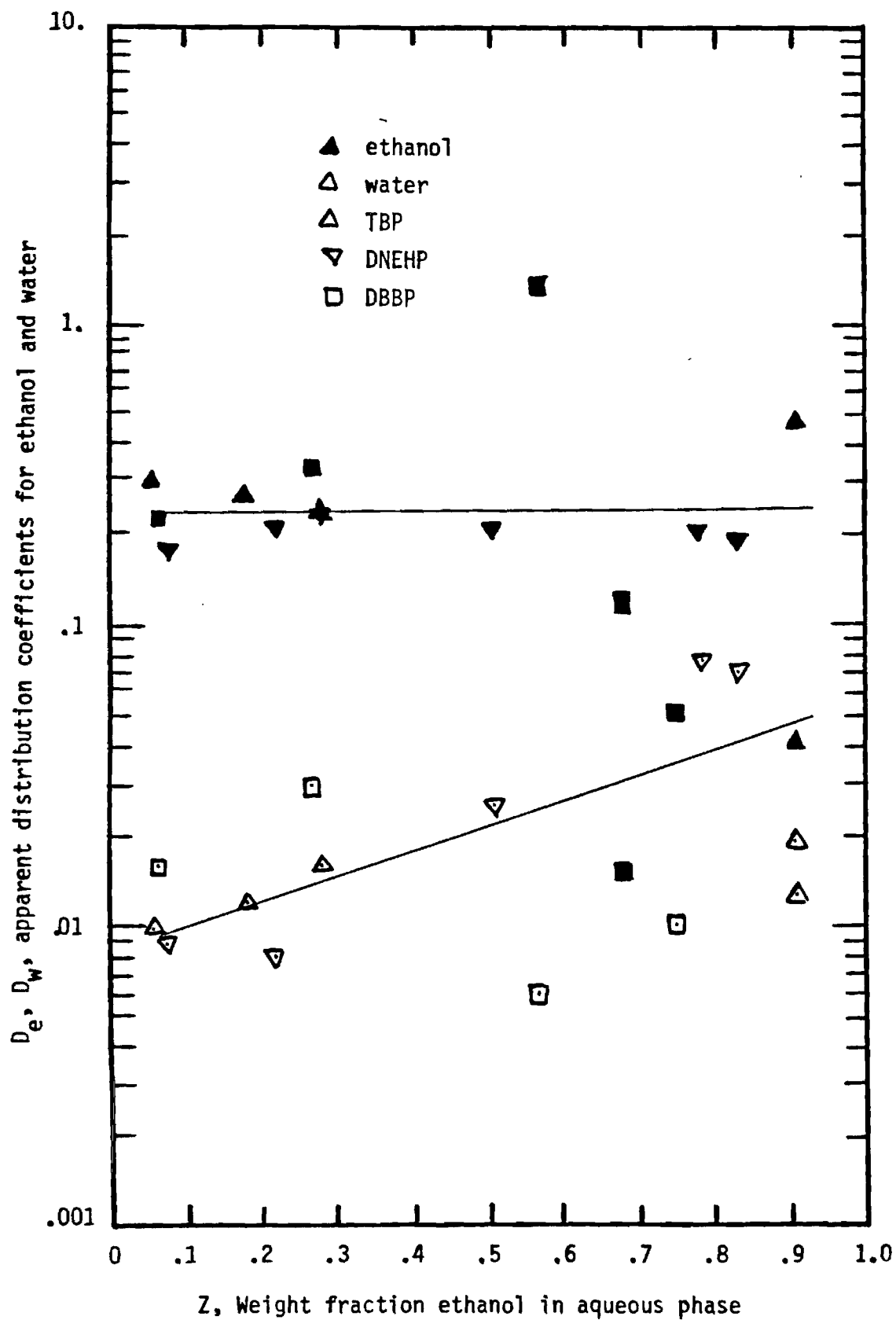| Compound	Soluble
I. Phosphates:	
Tributyl	Yes
Trineopentyl	No
Dineopentyl-2-Ethylhexyl	Yes
Trimethyl	No
Triethyl	No
Tricresyl	No
Tris(Butoxyethyl)	Yes
II. Phosphonates:	
Dimethylmethyl	No
Dibutylbutyl	Yes
III. Phosphinexoides:	
Triphenyl	No
Tricoctyl	No
Tributyl	--

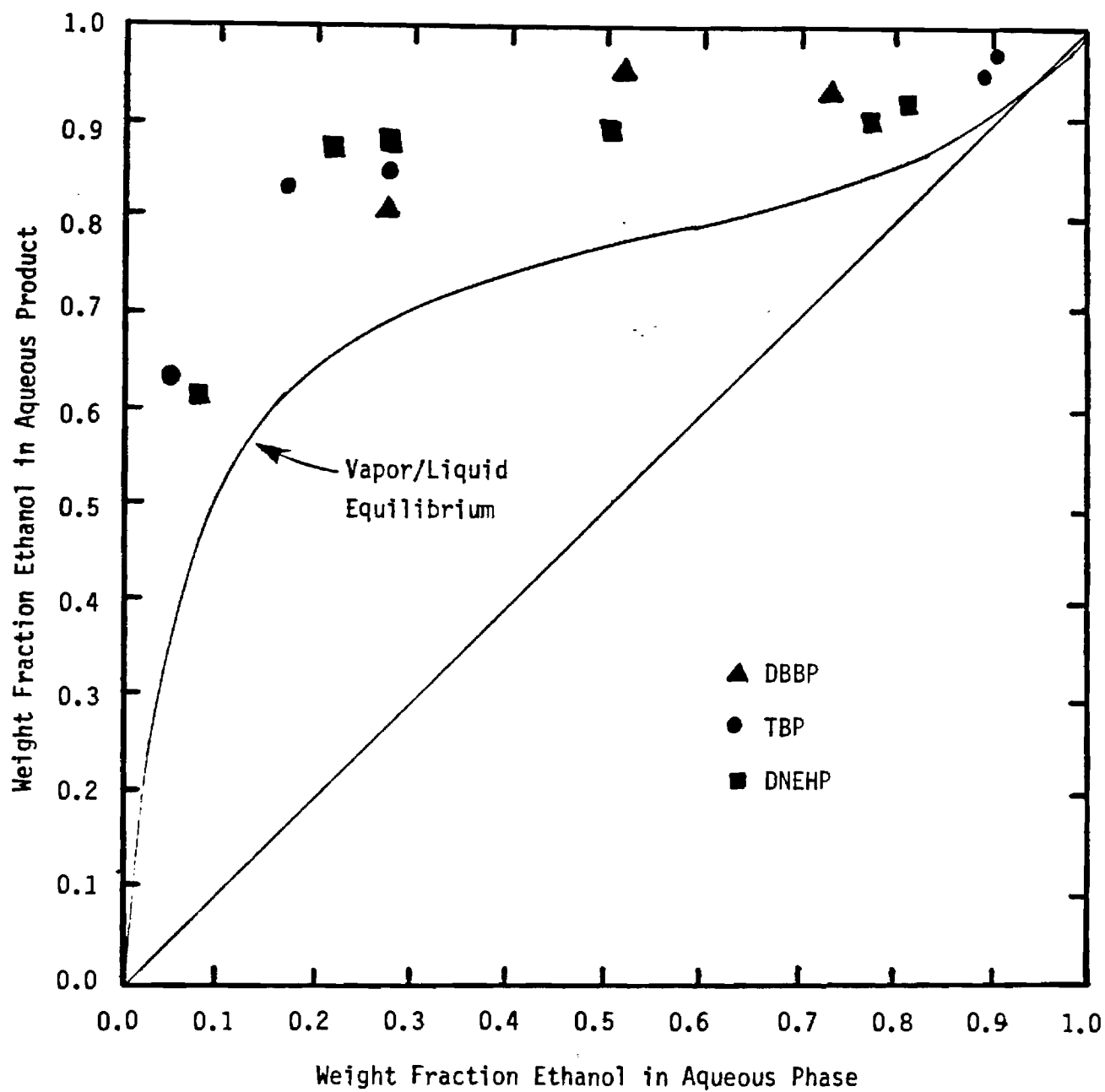Fig. 2. Distribution coefficients for ethanol and water using 1.1 $\underline{M}$ TBP, DNCHP, and DBBP in NDD.

Fig. 3. Distribution coefficients for ethanol and water using 1.1 M TBP, DNEHP, and DBBP in NDD.

Batch equilibrations for alcohols, esters and carboxilic acids have been carried out under slightly different conditions relative to those tests for the organophosphorous extractants. In particular, the stripping time has been reduced in some tests and the percentage of solute stripped calculated from the overall material balances for the equilibration. This check is possible since the phase densities before and after equilibration are also measured and the weight percentage ethanol was calculated from gas chromatographic (GC) analysis. In contrast, the extraction data shown in Figs. 2 and 3 result from conditions in which essentially all of the ethanol and water solutes were stripped from the high-boiling organics.

In most cases, about 25 mls of each phase were equilibrated. However, when the solvent loading was low (e.g., at dilute alcohol concentrations), then the solvent volumes may have been increased to 50 or 75 mls. In any event, initial and final weights and volumes were estimated. Consequently, four phase densities could be calculated and the overall material balances were be based on either the initial and final aqueous phase densities or, preferably, their ethanol weight fractions based on a GC analysis. In addition, the observer also attempted to measure those changes in organic an aqueous phase volumes that resulted from equilibration.

In some cases, the organic phase was clarified by either centrifugation or filtration. Subsequently, a stripping test consisted of weighing a measured solvent volume, stripping at a controlled temperature and pressure, and weighing the final volumes and weights of stripped organic and condensed product. In addition, the condensed product was examined for weight fraction of ethanol by density and either GC or NMR analysis.

Figure 4 summarizes the calculated ethanol and water distribution coefficients for the systems 2-ethylhexanol (2EHOH), Umbrex-n-fatty alcohol (UNFOH), tridecanol (TDOH), 2-ethylhexanoic and (2EHOOH)), and 3-heptanol (3HPOH).
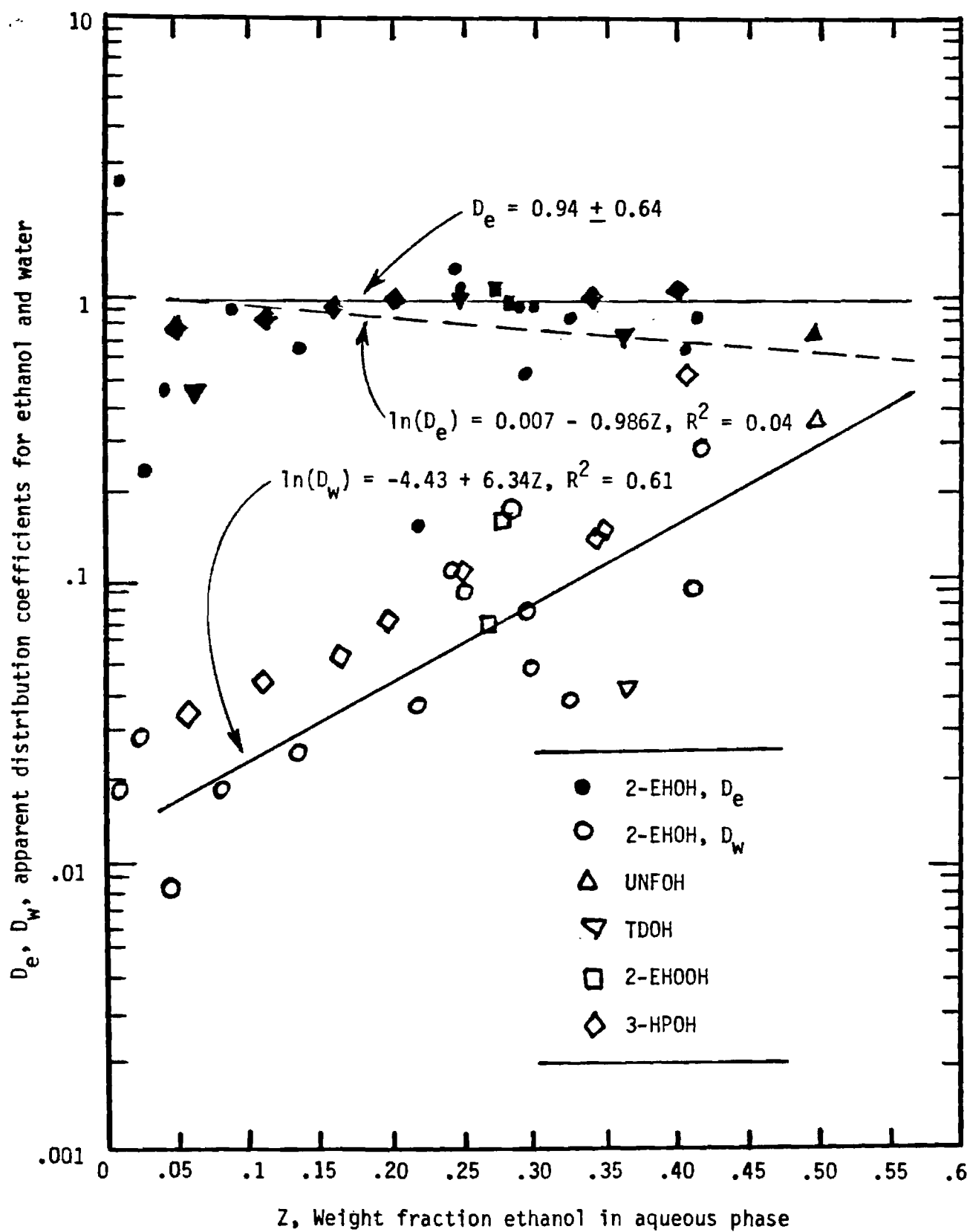
Fig. 4. Distribution coefficient data for several alcohols and 2-ethylhexanoic acid.

A statistically significant fit to the water distribution data is shown in Figure 4 with a squared correlation coefficient of 0.61. The correlation that appears in Figure 4 for the ethanol distribution coefficient is statistically insignificant compared to the alternative hypothesis that the ethanol distribution coefficient is independent of the weight fraction of ethanol in the acqueous phase at the 95% confidence level.

Figure 5 summarizes the same equilibration data as Figure 4, but in terms of the weight fraction ethanol in the condensed aqueous product versus the weight fraction ethanol in the raffinate.

The solvents examined appeared to give additional enrichment, compared to the vapor/liquid equilibrium curve, for all systems in Figure 5 except for n-butylacetate (NBUAC) and Umbrex-n-fatty alcohol (UNFOH). The tridecanol tests appeared to give the driest products. One measurement was in excess of 96 wt % and nine observations showed product compositions of greater than 80 wt % ethanol.
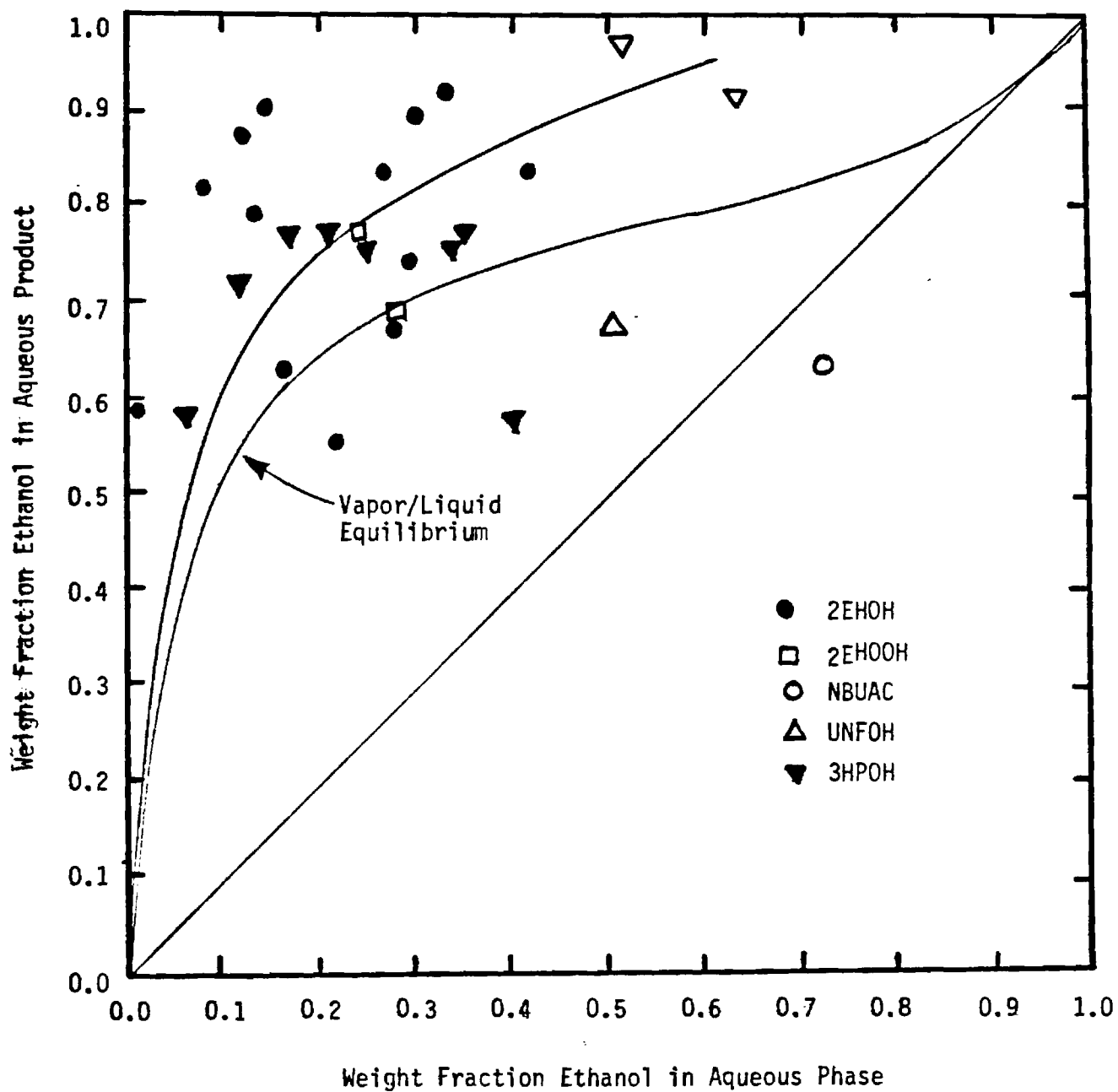
Fig. 5. Weight fraction ethanol in the aqueous product after stripping versus the ethanol weight fraction in the equilibrated aqueous phase for several alcohols and 2-ethylhexanoic acid.

1.3   Mutual Solubility Curves

The batch equilibration tests decussed in the previous sections represent an analytic method for determininig distribution coefficients. Alternatively, a synthetic method (6) may be used in which mixture cloud points are tritrated by adding successive quantities of either water and ethanol or else solvent and ethanol are added to induce and remove turbidity from either the saturated organic or else the saturated aqueous phase respectively. This procedure permits the calculation of the mutual solubility curve as is shown in Figure 6 for a solvent mixture consisting of 60 vol % tridecanol (TDOH) dissolved in n-dodecane (NDD). Given this curve, then tie lines may be established from solving the material balance equations for any two components to predict the weight ratio of the aqeous to the organic phase and graphically estimating this same ratio from the mutual solubility curve using the inverse-lever rule. By trial-and-error, tie lines can be found graphically such that the ratio from the material balance equations is approximately equal to that value which was calculated from the inverse-lever rule. Then the distribution coefficient and enrichment may be calculated as shown in Figures 7 and 8.
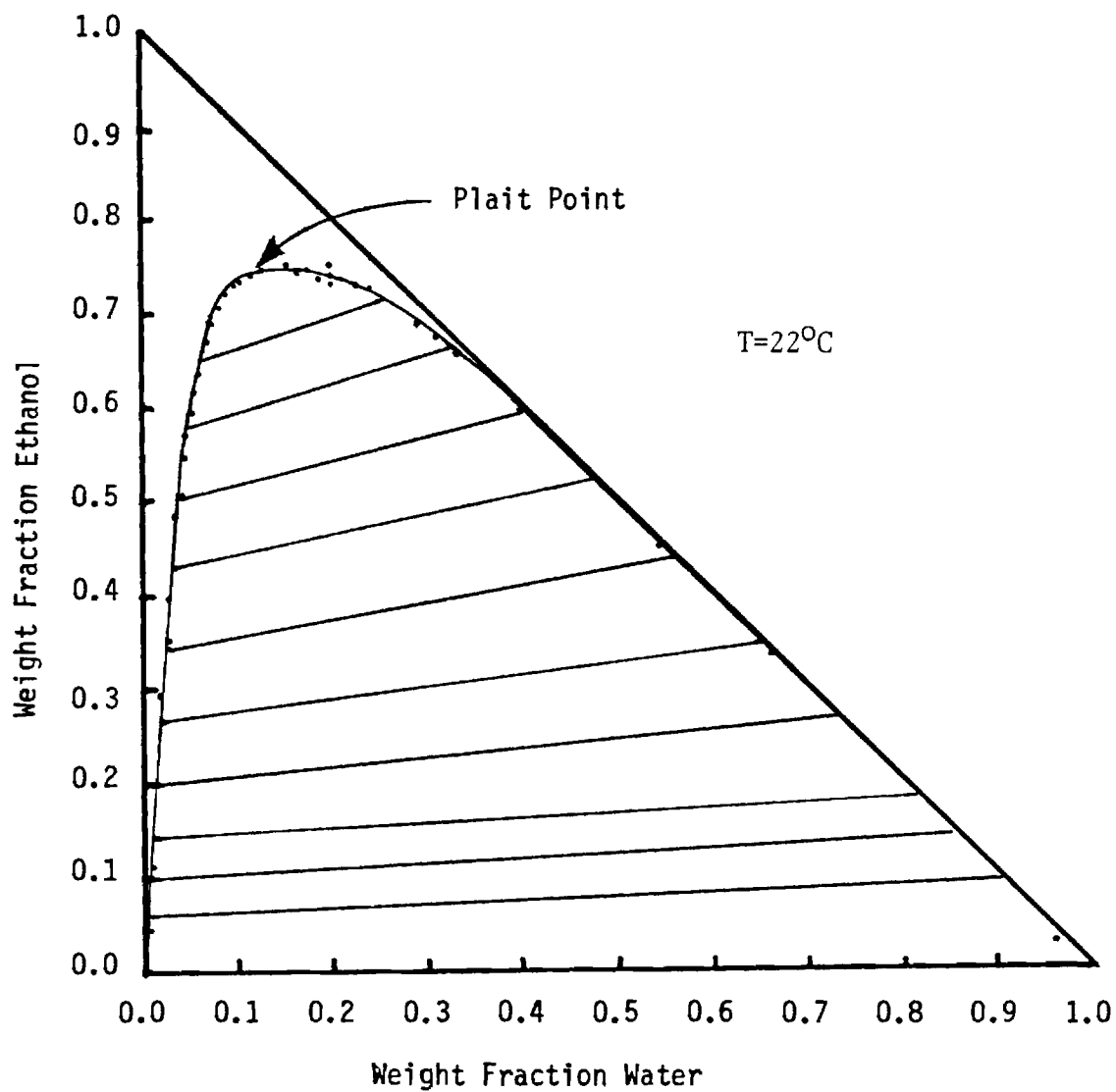
Fig. 6. The mutual solubility curve and several tie lines for the system water, ethanol, and 60 vol % tridecanol in n-dodecane.
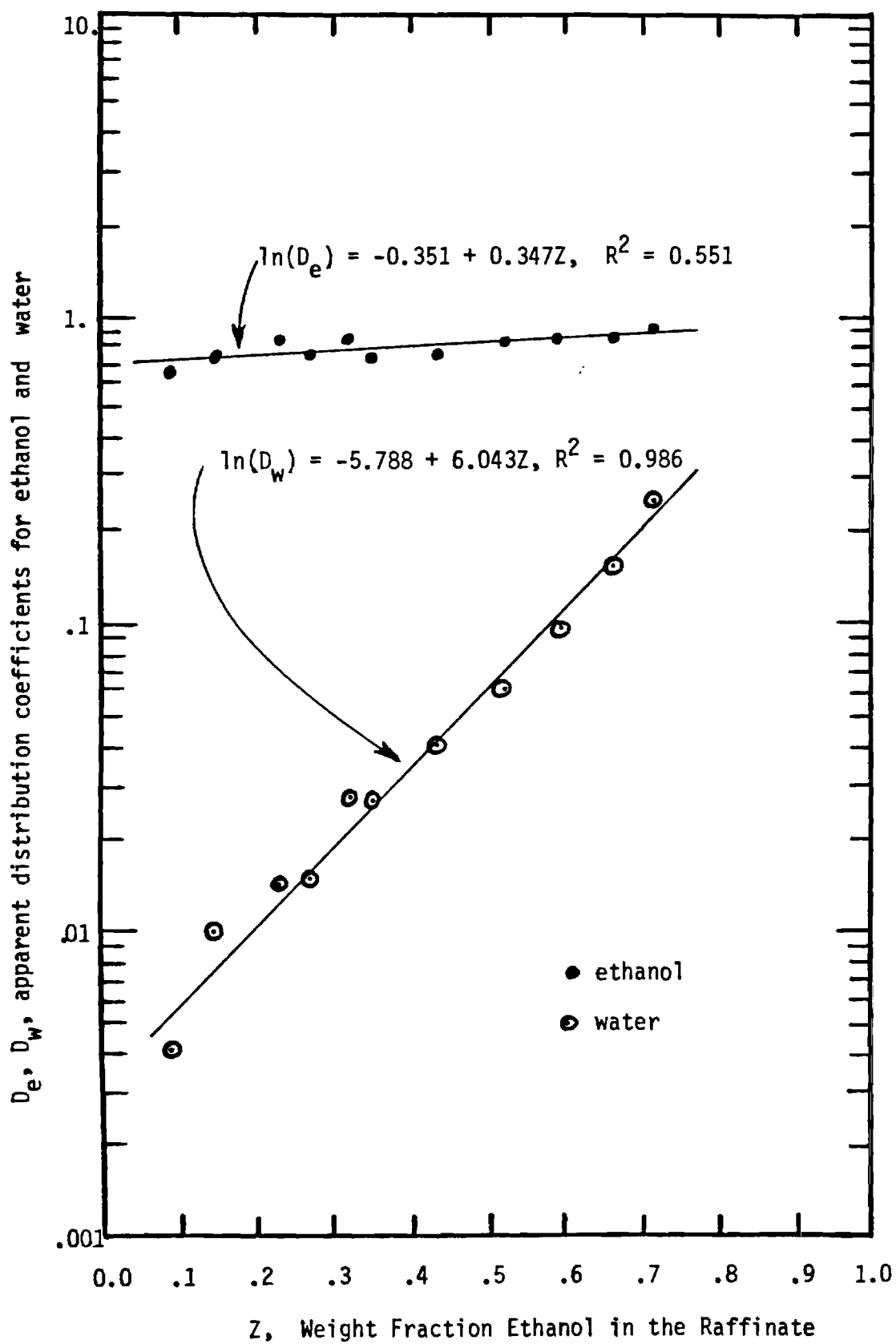
Fig. 7. Distribution coefficients for ethanol and water using the solvent 60 vol % tridecanol in n-dodecane.
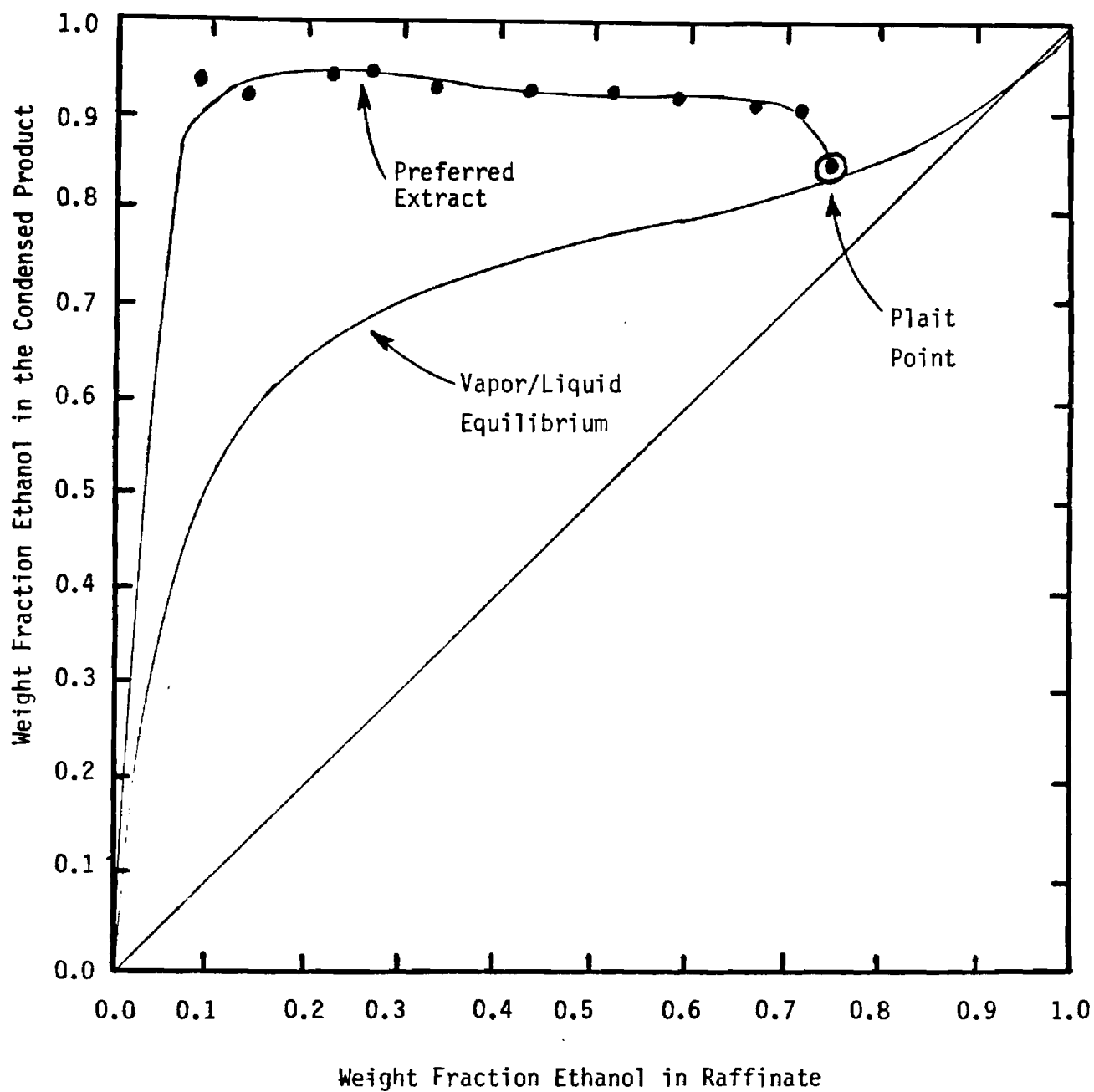
Fig. 8. Weight fraction ethanol in the condensed product after stripping the organic phase versus the weight fraction ethanol in the equilibrated raffinate using the solvent 60 vol % tridecanol in n-dodecane.

1.4   Stripping Tests

The batch equilibration tests described in Section 1.2 typically yielded 40 mls of organic sample that could be stripped to give measurable amounts of enriched ethanol in water mixtures. In addition, a series of laboratory experiments were conducted in order to determine the necessary operating conditions required to strip the ethanol out of the organic solution more precisely. These experiments were carried out using a solution of 4.66, 0.16, and 95.18 weight percent of ethanol, water, and 1.1 molar TBP-NDD respectively, with the TBP and NDD mixture being 38.59 weight percent TBP before addition to the ethanol-water solution.

The apparatus used to conduct these experiments is shown as Figure 1. A constant temperature bath was brought to the desired temperature and the sample flask put into place and allowed to come to equilibrium while the connecting stopcock to the vacuum supply was closed. After adjusting the air bleed on the vacuum supply in order to produce the desired vacuum, the glassware and tubing were warmed with a heat gun to prevent any condensation of the ethanol vapor before it reached the sample tube and any refluxing effect in the sample flask. This was repeated at intervals throughout the experiment.

Next, the stopcock between the flask and vacuum sypply was opened and the timer started. Upon reaching the end of a pre-determined time period, (e.g., 5 minutes) the timer was stopped as the stopcock was turned to cut off the vacuum supply, and hot air was blown on the glassware to try and recover any remaining ethanol vapor. Finally, the second stopcock was released to allow atmospheric pressure to re-enter the line leading to the sample collection tube and the tube was removed from the dry ice-acetone bath and replaced with another one. The vacuum was then allowed to build up in the tubing and the stopcock opened again as the timer was re-started. This entire procedure was

then repeated at the end of the next time interval, and the experiment continued until samples collected over a long time interval became miniscule.

The results of these experiments indicated that most of the ethanol is stripped out of the solution within the first 10 minutes of the process. After a total stripping time of from one to two hours, so little additional ethanol was recovered that the system was considered to be at equilibrium. The fraction of the original ethanol stripped out of solution is shown in Table 3, for the four conditions of the different experiments.

Table 3. Percentage ethanol stripped at equilibrium condition for several temperatures and pressures.

| Temperature (°C)	Pressure (mmHg)	% ETOH Stripped at Equilibrium
35	20	57.6
35	10	79.9
50	20	84.4
50	10	89.2[a]

[a]The rapid effevescence of ethanol and water resulted in some losses. This is a projection based upon a 9% loss.

1.5 Synthesis of Ethanol Extraction Agents

In order to more fully understand the capability of various functional groups and combinations of functional groups in the selective complexation of ethanol, the following materials have been synthesized for evaluation.
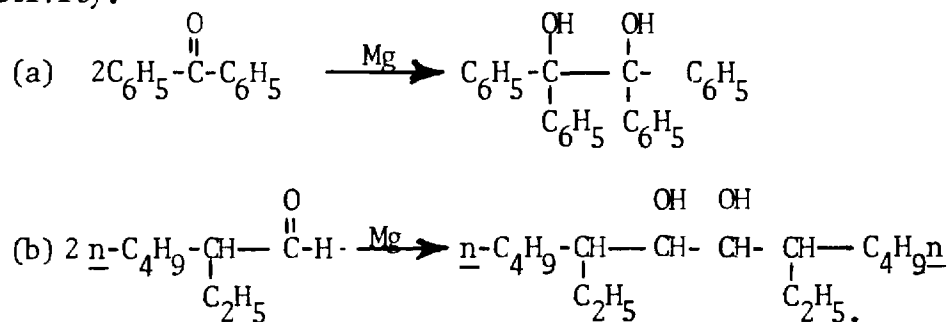
1. Oximes

The oxime represents a functionality capable of hydrogen bonding at three centers - nitrogen, oxygen and hydrogen. The following two oximes have been synthesized. In each case a different hydrophobic - hydrophilic balance has been achieved.

(a)

(b) $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3 + H_2N-OH \xrightarrow{H+}$ $+H_2O$
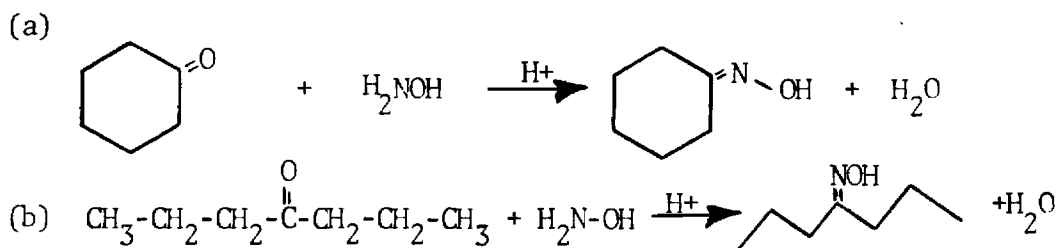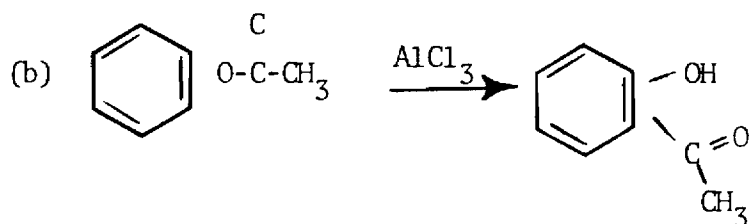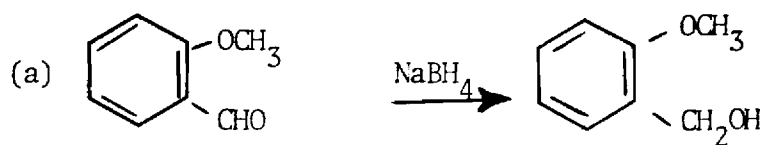
2. 1,2-Diols

1,2-Diols represent a multisite hydrogen bonding molecular fragment which may be synthesized by a relatively facile bimolecular reduction process involving aldehydes and ketones. Various hydrophobic substituents attached to the 1,2-diol fragment impart hydrocarbon solubility and ethanol selectivity.

(a) $2C_6H_5-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow{Mg} \underset{\underset{C_6H_5\ \ C_6H_5}{|}}{C_6H_5-\overset{OH}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}-C_6H_5}$

(b) $2\ \underline{n}-C_4H_9-\underset{\underset{C_2H_5}{|}}{CH}-\overset{O}{\overset{\|}{C}}-H \xrightarrow{Mg} \underline{n}-C_4H_9-\underset{\underset{C_2H_5}{|}}{CH}-CH-\ CH-\underset{\underset{C_2H_5.}{|}}{CH}-C_4H_9\underline{n}$

3.   o-Methoxybenzyl alcohol and o-hydroxy acetophenone

o-Methoxybenzyl alcohol and o-hydroxy acetophenone represent multiple bifunctional hydrogen bonding species with high hydrocarbon solubility.

(a)

$$\text{(benzene ring with } -OCH_3 \text{ and } CHO) \xrightarrow{\text{NaBH}_4} \text{(benzene ring with } -OCH_3 \text{ and } CH_2OH)$$

(b)

$$\text{(benzene ring with } O\text{-}C\text{-}CH_3) \xrightarrow{\text{AlCl}_3} \text{(benzene ring with } -OH \text{ and } C=O, CH_3)$$

2.   Discussion

The initial studies focused on the use of organophosphorous compounds as extractants. Our continuing studies (7,8) of the mechanisms of water extraction into substances such as 30 vol % TBP in n-dodecane suggest that one or more dimerization mechanisms exist whereby water may coordinate with two or more TBP molecules to form aggregates that are soluble in the diluent. In the system water, TBP, uranyl nitrate and diluent, for example, statistical analysis suggests that water extracts almost exclusively by a single mechanism whereby three or four water molecules associate with two TBP molecules to form an extractable complex.

If this mechanism occurs exclusively for the case of water extraction into TBP and diluent in the presence of ethanol, then the separation factor (1) for ethanol should approach infinity as the ethanol weight fraction in the equilibrated aqueous phase goes to unity. Our experimental evaluations with TBP extracting both water and ethanol show the opposite trend.

This difference may be attributed to the fact that water and ethanol associate with each other. This situation can give rise to additional mechanisms, such as the extraction of an ethanol-water complex by TBP, which do not exist in the system water, TBP, uranyl nitrate and diluent alone. Consequently, we see a decrease in the separation factor because the water is carried into the organic phase due to its association with ethanol.

Infrared studies (7) suggest that in the liquid state, ethanol is largely dimerized. Also, the hydroxyl groups have an affinity for each other so that Trouton's constant for ethanol is about 26.9 rather than 21 cal/mole $^{\circ}$C, as for unassociated liquids. In fact, the affinity of an ethanol molecule for another of its kind is somewhat greater than its affinity for water due to the electronic characteristics of the ethyl substituent. Consequently, we find that terminal

alkyl alcohols are better extractants for ethanol than neutral organophosphorous extranctants. Alcohols like 2-ethylhexanol are superior to neutral organophosphorous compounds because ethanol prefers their hydrogen bonding characteristics over water and, therefore, this alcohol exhibits a distribution coefficient, D_e, close to unity. On the other hand, 1.1 $\underline{M}$ mixtures of TBP, DNEHP and TBP in n-dodecane exhibit average D_e values around 0.25.

Figures 2, 4 and 7 compare the apparent distribution coefficients for ethanol with those for water as a function of the weight fraction of ethanol in the raffinate. Although there is a considerable amount of noise in Figures 2 and 4 due to the analytic experimental techniques, all three figures exhibit trends that show a characteristic difference between ethanol and water and the way in which these solutes interact with the solvents. In particular, the ethanol distribution coefficient appears to be almost independent of the ethanol. This difference suggests that ethanol migrates toward the organic phase primarily through its attraction to the solvent whereas water migrates primarily due to its affinity for the ethanol in the extract.

Based on these observations, we have revised our strategy for the synthesis of an effective ethanol extractant. We want a substance which contains one or more hydrogen bonds that appear highly attractive to ethanol, but which exist in an environment that is sufficiently shielded from water to yield both adequate solvent capacity and selectivity. One candidate which we believe may have such superior properties is the molecule 5,8-diethyl-dodecyl-6,7 diol which is readily synthesized from 2-ethylhexanol. We are also planning tests on several aromatic alcohols, such as diisopropyl benzyl alcohol and several aliphatic oximes which may exhibit improved characteristics.

The selective extraction of alcohol from fermentation liquors involves a delicate balance of several molecular structural characteristics. The scouting tests that are summarized in Table 1 appear useful for an initial screening of

extractants, but they are not conclusive in themselves. A useful solvent should show a measurable increase in volume when contacted with 60 vol % ethanol, a decrease in the refractive indices for both phases, relatively clear equilibrium phases and rapid disengagement (< 2 min.) without centrifugation. Substances that appear most favorable (e.g., tridecanol) also tend to be more viscous and exhibit long disengagement times. In some cases, a nearly stable emulsion may collect at the interface that occupies about 10% of the total volume of both phases.

Scouting tests are also useful in that they quickly reveal the formation of a third phase and problems with phase disengagement. However, measurements are more difficult at low ethanol concentrations (i.e., 5 to 25%) although these conditions are of primary interest with respect to cascade operations. In addition, there have been some problems with reproducibility. For example, the measured acqueous and organic refractive changes are $-.0428 \pm .0541$ and $-.00945 \pm .00292$ for 2-ethylhexanol when it is equilibrated with 60 vol % ethanol. There appears to be a preferential extraction of ethanol which is confirmed by the batch equilibration studies, but the magnitude of these deviations alone is not really adequate to assess the relative merits of alternative systems such as in test 6-8, 13-14, and 18-22 with a high degree of reliability. On the other hand, negligible changes in volumes and indices upon equilibration with 60% ethanol do appear to be sufficient cause, when considered together, to discontinue the further evaluation of a particular solvent system. Thus, the scouting tests are useful for the elimination of candidate extractants, but are less reliable in establishing the relative merits of alternative systems when both exhibit roughly equal solvent phase volume increases and the refractive changes lead to the same conclusion (see Table 4) that more ethanol than water extracted.

The direct measurement of ethanol and water distribution coefficients via the techniques described in Section 1.2 have several advantages. They permit

Table 4. Commonly observed refractive changes during scouting tests.

| Case | Refractive Index Changes[a] | | Conclusions |
	Aqueous	Organic	
1	0	0	No phase transfer occurred
2	0	-	Equal amounts of water and alcohol extracted
3[b]	-	-	More ethanol than water extracted
4[c]	+	-	More water than ethanol extracted and/or the solvent is water soluble
5	+	0	The solvent is water soluble, but does not extract

[a]All cases are subject to cancellation of changes, or else change reversals, due to high solvent solubilities in the aqueous phases. In these cases, the aqueous phase is hazy after equilibration or else becomes hazy when it is subsequently diluted with water.

[b]This is the most favorable case.

[c]This case is ambiguous.

identification of third phase formation and disengagement problems. In addition, sufficient quantities of solvent are equilibrated so that a measurable amount (2-15 gms) of condensed product can be recovered using the apparatus shown in Figure 1. Thus, the test permits an evaluation of the percentage of product stripped as well as the product composition measured by density, NMR and/or GC analysis.

On the other hand, the batch equilibration tests are relatively slow, only yield one value for D_e and D_w per test, and are difficult to reproduce because the calculated material balances are based upon four to six different measurements which all contain random errors. Moreover, a comparison of the scatter in Figures 2 and 4 with that in Figure 7 clearly shows that the synthetic method described in Section 1.3 yields more reliable distribution coefficient estimates. The distribution coefficients for 3-heptanol (3HPOH) in Figure 4 appear to have about the same degree of accuracy as the data in Figure 7, but the 3-heptanol coefficients were calculated from results presented by Ovalline and VanWinkle (8) who also used the synthetic method as described by Othmer, White and Trueger (6).

Insofar as the two titrations yield the entire mutual solubility curve, the synthetic method is preferable to the analytic method for the estimation of water and ethanol distribution coefficients. The tie lines can be readily generated from the curve by trial-and-error using a hand-held programmable calculator such as the TI-58. On the other hand, these titrations yield no information concerning the formation of a third phase, problems in phase disengagement, or the ease of product stripping. Therefore, the synthetic method yields necessary information, but it is not sufficient in itself to adequately characterize a candidate extractant.

The stripping tests suggest that some preheating of the extract before stripping may be required before an adequate degree of product removal can be achieved. Moreover, conceptual studies (9) suggest that vacuum distillation is

more economical than carrier gas stripping or solar stills and that substantial extract preheating can be achieved through heat rejection from the refrigeration cycle (10) that is required to condense the product. In this regard, the higher solvent loadings that appear attainable using several of the high-boiling alcohols which we have examined will also result in higher extract temperatures before stripping than were calculated (10) in the earlier work.

In summary, the system 60% tridecanol in n-dodecane appears capable of producing an 94% product using about 50% reflux and an organic-to-aqueous flow ratio of about 1.67 at the raffinate end of the column. As shown in Figure 9, the organic-to-aqueous flow ratio is only about 2.2 near the column raffinate, rather than being close to ten as was calculated (1) earlier. On the other hand, the estimated product composition is only 94 wt % based on Figure 6. However, the data in Figure 6 should still be regarded as preliminary since the initial cloud points are easily over titrated and since we have measured several other product compositions that were in excess of 96% ethanol using pure TDOH. Since the addition of n-dodecane should increase the product quality, this experimental inconsistency has yet to be resolved.

Significant experimental progress has been made in terms of rapidly identifying the properties of a candidate extractant. The preferred steps in evaluation currently are as follows:

1.   Perform a scouting test to qualitatively establish the solvent characteristics.

2.   Titrate the mutual solubility curve and calculate the distribution coefficients and the equilibrium conditions that maximize the weight percentage ethanol-to-water ratio in the organic phase.

3.   Perform one or more batch equilibrations to evaluate the solvent performance as a drying agent.
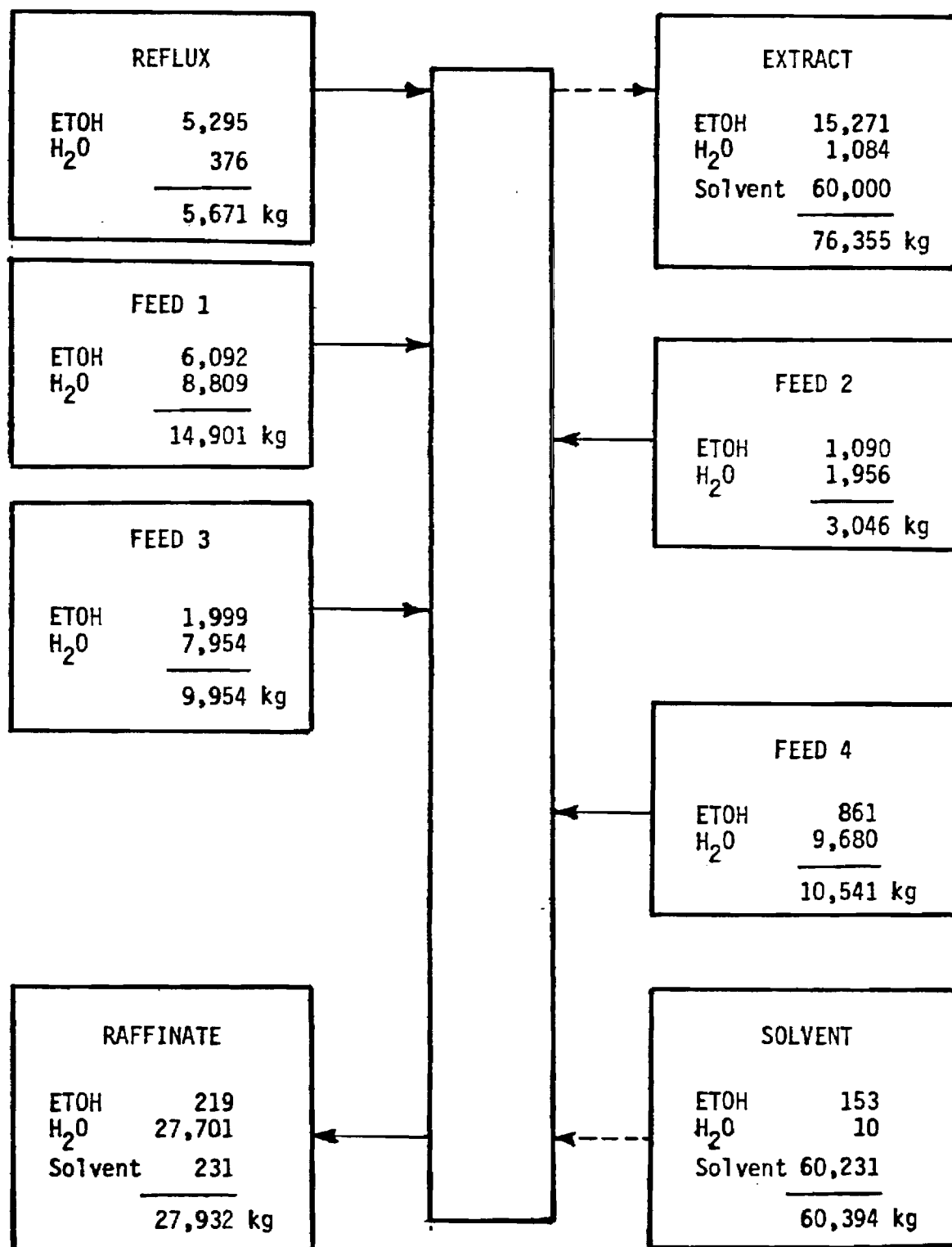
Fig. 9. Conceptual flowsheet for recovering ethanol from vacuum fermentation(5) effluents using 60 vol % tridecanol in n-dodecane. This configuration requires thirteen theoretical stages.

4.   Perform stripping tests of the extract using the
most favorable composition that results from the
mutual solubility curve.

Although the ultimate product quality that can be achieved via solvent extract-
ion remains in doubt at this time, it seems probable that the product quality
can exceed 94 wt % ethanol using a number of solvent systems. The recovery
costs in this case would be substantially less than 50% of those resulting from
distillation.

Replicate experiments are planned in the near future for the system 60%
TDOH in NDD and the species 5,8-diethyl-dodecyl-6,7 diol (DDD). If a minimum
product purity ($\geq$ 96%) can be confirmed experimentally, then counter-current
extraction tests will be initiated using separatory funnels. Favorable results
within the next two months will facilitate a continuous bench-scale demonstra-
tion early in FY-82 as originally (1) planned.

3. Acknowledgements

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