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FINAL REPORT

FEASIBILITY OF A NOVEL LOW-ENERGY EXTRACTION PROCESS
FOR SEPARATING ETHANOL AND WATER USING CONJUGATING SOLUTIONS

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ABSTRACT

The overall objective of this project phase was to investigate the feasibility of a novel low-energy extraction process for separating ethanol and water using an extractant that forms a conjugating binary with ethanol. The extractant is chosen to be miscible in ethanol in all proportions at temperatures of about 75°C and above but only partially miscible below this temperature. Also, the extractant is chosen to be immiscible in water.

In the proposed scheme hot extractant is contacted with the ethanol-water feed solution to extract ethanol. After equilibration, the extractant which would not contain ethanol, would be separated from the ethanol-water solution by forming a separate phase because the extractant and water are immiscible. The extractant-ethanol solution will then be cooled below the solution consolute temperature to separate into an extractant-rich solution, that is recycled back to the extractor section, and an ethanol-rich solution, which is the final product.

The specific technical tasks under this study dealt with (i) the identification of the most promising extractant, (ii) the determination of binary and ternary phase composition data, and (iii) the design and analysis of a baseline system using the proposed technique.

The project started with the search for a suitable extractant that can extract a part of ethanol in the feed solution. A number of compounds which exhibited conjugate behavior with ethanol were identified. From this list the three most promising candidates: hexadecane, cottonseed oil and white light paraffin oil, were identified. Based upon the binary phase data it was found that ethanol-paraffin oil offered the best separation characteristics. The upper critical solution temperature for this binary was found to be 105°C. Consequently, experiments were done to determine the necessary phase composition data for the ethanol-water-paraffin oil ternary system both at 115°C (the temperature of the extraction process) and at 30°C (the temperature of the ethanol/extractant separation process). The experimental data indicated that the proposed scheme can produce ethanol with less than one percent water concentration.

Based upon the results of the experimental work, a flow diagram for the baseline system of 5 million gallons per year was prepared. The final product contained 94.7% ethanol, 4.5% oil and 0.8% water by weight. Total thermal energy required for different configurations (depending upon the product reflux rate and concentration of ethanol in the feed solution) was estimated to be 4 to 34% of the final product fuel value. For the baseline case with a reflux of 3% and 30% ethanol solution feed, the total thermal energy required was estimated to be about 7.3% of the product fuel value. The extraction column for this case was estimated to be 22 feet high and 12 feet in diameter with a total of 11 stages.

Since paraffin oil is in the fuel oil range and has a fuel value about twice that of ethanol, the final product containing 4.5% oil and 0.8% water can be directly used as a motor grade fuel. It is believed that the proposed system will be simpler and less expensive than the conventional distillation system producing the same quality product. In particular, because of no phase change and modest operating temperatures and pressures, all the heaters and heat exchangers should be relatively inexpensive. It appears plate heat exchangers designs developed for geothermal and ocean thermal energy conversion should be useable with the exception that the material requirements will be less stringent for the proposed system. Further work is needed to size the major equipment items and to carry out a detailed cost and energy comparison of the proposed system with the conventional distillation system. All the equipment required for this process is believed to be state-of-the-art and does not need any major development effort.

1.0 INTRODUCTION

The production of ethanol from food carbohydrate commodities takes place in two separate broad steps: 1) fermentation of the carbohydrate saccharified in aqueous infusions; and 2) separation and purification of the ethanol from water and fusel oils. One important question surrounding the production of ethanol for fuel use from agricultural feedstock via fermentation is the energy required in separating and purifying the ethanol from the fermentation mixture.

In the conventional distillation process, the beer containing 5-15% ethanol resulting from the fermentation is transferred into a beer still. The overhead from the beer still is about 95% ethanol, along with the fusel oil. The bottoms from the beer still has a solids content of 2-14%, and can be used as animal feed after evaporation. To produce gasohol, the 95% ethanol must be purified further. To break the azeotrope of about 5% (actually 4.43%) water and 95% ethanol, a third component is usually added, and 99.5% pure ethanol can be produced from a dehydrating still. Since the vaporization-condensation steps inherent in distillation each involve the addition and then the subsequent removal of about 1,500 Btu in and out for each pound of water processed, the energy required is considerable.

In a modern, well-designed, energy efficient farm scale ethanol plant, the energy required to obtain 192-proof ethanol is about 15,300 Btu/gal of 95% ethanol (1). Further purification of alcohol to produce 199-proof product is energy intensive and requires significant amount of additional energy. Overall, state-of-the-art distillation processes require between 20,000 and 40,00 Btu/gal of ethanol, i.e., about 25 to 50 percent of the combustion energy of the product ethanol. Needless to say, the Saccharification and fermentation steps also consume some energy. The energy balance issue is of great concern, and it would obviously be beneficial to develop a more energy-efficient method of separating and purifying the ethanol product than distillation.

1.1 Description of the Proposed Process

One possible means of separating the ethanol product resulting from fermentation is the use of liquid extractant. The liquid extractant would be contacted with the fermentation mixture. A fraction of the alcohol in the fermentation mixture would be transferred into the extractant phase. The extractant, being essentially insoluble in water, would then be separated from the fermentation mixture by simple settling. The problem then would be how to separate the ethanol from the extractant. Distillation could be used, but this was the operation to be avoided in the first place (although the alcohol/extractant distillation could be easier).

One attractive way of separating ethanol from the extractant is to choose an extractant which forms a conjugate solution pair with ethanol. Two liquid chemical species can be completely miscible within one temperature range but only partially miscible or practically immiscible if the temperature is changed. This process is exemplified in Figure 1 by solutions of ethanol and cottonseed oil, which are completely miscible at any temperature above 70°C. Below 70°C (which is called the upper critical solution temperature, UCST) in general, a mixture of ethanol and cottonseed oil will divide into two solutions, one rich in ethanol and the other rich in cottonseed oil whose equilibrium compositions are fixed by the temperature. Such coupled solutions are called conjugate solutions, and the unmixing process by which they are formed is called conjugation. Thus, for example, a mixture with an overall composition of 50% ethanol and 50% cottonseed oil will form two equilibrium solutions at 30°C, one containing 5% oil and 95% ethanol and the other containing 88% oil and 12% ethanol.

A number of organic liquids including higher hydrocarbons and vegetable oils form conjugate solution pairs with ethanol, and may be possible extractants for a conjugating extraction process for separating ethanol and water. An example flow sheet for a conceptual process is shown in Figure 2. Figure 1 shows a conceptual phase diagram for mixtures of ethanol and, for example, cottonseed oil.

To illustrate the performance of the proposed process for separating the alcohol from the fermentation mixture, hot cottonseed oil (stream 1 in Figure 2 and point 1 in Figure 1) would be contacted with the beer feed solution (stream 6 in Figure 2) to extract the alcohol. Both streams would be heated above the UCST of the ethanol/cottonseed oil mixture (see Figure 1). After equilibrating with the beer solution, the cottonseed oil, which would now contain ethanol, would be separated from the beer solution by forming a separate phase in the separator because cottonseed oil and water are immiscible. Although Figure 2 shows only one theoretical stage of equilibration and subsequent settling, it would be more efficient to use a continuous extraction process, which would remove a larger fraction of the alcohol from the water phase. The cottonseed-oil ethanol mixture (stream 2 in Figure 2 and point 2 in Figure 1) would then be cooled below the UCST (stream 3 and point 3) to separate into a cottonseed oil-rich solution (stream 4 and point 4) and an ethanol-rich solution (stream 5 and point 5), which is the ethanol product.

The cottonseed oil-rich solution (stream 4 and point 4) would be heated and recycled to the extractor to pick up more ethanol. If the ethanol-rich solution is pure enough, perhaps it could be used directly for blending with gasoline as motor fuel, depending upon the residual cottonseed oil and water content in the product stream 5.

1.2 Potential Advantages of the Proposed Scheme

In separating and purifying the alcohol with the proposed process, there will be no change of phase which is generally associated with a significant input of thermal energy as latent heat. Only sensible heat input will be required. In addition, a significant part of the required sensible heat input can be recycled through heat exchange with the mixture as it is cooled down to separate the conjugate solutions. It is expected that the energy requirement should be about a factor of 3 to 6 lower than that for conventional schemes. Secondly, the heater, cooler and the heat exchanger required for the proposed scheme will be simple in design requiring inexpensive plate heat exchangers rather than a boiler and a condenser in the distillation schemes.

1.3 Objectives of the Project

The overall objective of the work in this phase was to investigate the feasibility of the proposed low-energy extraction process for separating ethanol and water using an extractant which forms a conjugating binary with ethanol.

The purpose of this initial research was to try to identify the most appropriate liquid extractant and to evaluate the economics and the energy requirements of the proposed scheme for alcohol/water separation. This work involved several tasks. In the first task, the literature was systematically searched for the purpose of finding appropriate extractants. Promising candidates were analyzed according to the criteria developed under this task. Safety characteristics of the extractant were also to be considered.

Experimental work was then done on promising candidates to obtain the necessary binary phase data at room temperature. The extractant which showed the maximum potential was further tested in the laboratory and the experimental work included the following:

1. Determination of ethanol-extractant binary phase diagram
2. Determination of ethanol-extractant-water ternary phase diagram at 30°C and at a temperature about 15°C higher than the upper critical solution temperature for ethanol-extractant solution

In another task, the experimental data was used to develop a flow sheet for the baseline system. Material and energy balance equations were used to analyze the overall performance of the complete process. Under this task the cost and energy requirements of the proposed system were compared with the conventional distillation systems. The final task was concerned, of course, with project management and report preparation.

1.4 Project Summary

Selection of the Extractant

The project started with the search for a suitable extractant that can extract a part of the ethanol in the feed beer solution. This search began with the development of criteria for the identification of promising candidates. The most important of these criteria was that the extractant-ethanol binary should exhibit a partially miscible behavior with an upper critical solution temperature in the range of 60 to 100°C.

Although the criteria were useful for screening the candidate extractants, given the experimental data, these were not helpful in predicting the existence of suitable candidates. At present, to our knowledge, there is no theory or even correlation to predict the existence or properties of conjugate binary liquid systems. The search for the extractant, therefore, had to be based on those systems for which some data existed in the literature-typically only the UCST.

A number of candidate extractants which exhibited conjugate behavior with ethanol were identified. These could be grouped into three categories: C₁₂ to C₁₆ paraffins, vegetable oils and a list of speculative compounds, including paraffin oils, for which no relevant literature data could be found. From this list the three most promising candidates which were chosen for further screening included hexadecane, cottonseed oil and white light paraffin oil.*

While hexadecane was very attractive because it had the lowest UCST, 49°C, of the three compounds, however based on binary phase data, it was found that ethanol-paraffin oil offered the overall best separation characteristics at room temperature. Consequently, a series of experiments was planned to test the applicability of white light paraffin oil as the extractant for the proposed scheme.

*The white light paraffin oil purchased from Fischer Chemical Company had the viscosity value of 125-135 Saybolt. For brevity it is referred to as 'paraffin oil' in the rest of the report.

Binary and Ternary Phase Data

Experiments were done to determine the binary phase diagram for ethanol-paraffin oil system. The UCST for this binary increased from 105⁰C to 110⁰C when the moisture concentration in ethanol was increased from 0.2% to 1.0%. The effect of moisture in ethanol on the binary phase diagram was also investigated. Based on binary phase data it was evident that at 30⁰C this binary system has almost a complete separate particularly when the system contains a small amount of moisture.

To evaluate the performance of the proposed scheme it was necessary to generate the ternary phase data for the ethanol-water-paraffin oil system both at 115⁰C (the temperature of the extraction process) and at 30⁰C (the temperature of the alcohol/extractant separation process). Based upon experimental results at 30⁰C it was found that (i) the product from the proposed scheme will contain about 94.7% ethanol, 4.5% paraffin oil and 0.8% water by weight, and (ii) the extractant stream will contain about 96.5% paraffin oil, 3.47% ethanol and 0.03% water for recycling back into the system. Based upon ternary phase data at room temperature (18.4⁰C), it was also found that if the separation process operates at a lower temperature, the quality of the two streams would be further improved.

Design of the Baseline System

As a result of analyzing the binary and ternary phase data the original conceptual flow sheet was modified. In particular, the single-stage extraction subsystem was replaced by a continuous column comprising of an enriching and a stripping section. Also, a fraction of the ethanol product was recycled back to the extraction subsystem. Both these modifications were necessary to improve the quality of the product alcohol from the proposed scheme. To develop the flow sheet for the baseline system mass and energy balance equations were developed. Standard procedures were used to estimate the number of stages and the amount of extractant required for the design of the extraction subsystem for different feed concentrations. The total thermal energy required for different configurations as a fraction of the combustion value of the final product was also calculated.

For the baseline system of 5 million gallons per year capacity, with an on-stream factor of 90%, and a feed rate of 23,300 lb/hr of 30% ethanol solution, the total thermal energy required was estimated to be 7.3% of the final product fuel value. The final product contained 94.7% ethanol, 4.5% paraffin white light oil and 0.8% water by weight. The extraction section of the baseline system is estimated to have a total of 11 stages of which 2 will be in the enriching section and 9 in the stripping section. The size of the extraction column is estimated to be 22 feet high and 12 feet in diameter. However, there is a lot of uncertainty in the design of this subsystem because of a lack of any performance data. Other details about the baseline system are provided in Section 4.0.

In summary, it can be concluded that:

1. The proposed novel system offers the potential of an inexpensive energy-efficient scheme to separate ethanol-water mixtures.
2. For the baseline case with a reflux of 3% and a feed of 30% ethanol solution, the total thermal energy required is estimated to be 7.3% of the product fuel value.
3. Since paraffin oil is in the fuel oil range and has a fuel value about twice that for ethanol, the final product from the proposed scheme containing 4.5% oil and 0.8% water can be directly used as a motor grade fuel.
4. It is believed that the proposed system will be simpler and less expensive than the conventional distillation system producing the same quality product.
5. Because of no change in phase (like in evaporation and condensation), and modest operating temperatures and pressures, all the heaters, the cooler, the heat exchangers and the phase separator will be inexpensive. We propose that the plate heat exchangers developed for geothermal and ocean thermal energy conversion should be used in the proposed scheme.
6. In absence of any performance data controlled laboratory experiments are necessary to properly size and design the alcohol extraction and the phase separation subsystems. Only then a realistic cost and energy comparison of the proposed scheme with the conventional distillation process can be made.

2.0 SEARCH FOR SUITABLE EXTRACTANTS

2.1 Criteria for Selection of Appropriate Extractants

The key to the success of the proposed concept is to find a suitable extractant for the process. The extractant must meet a number of criteria, the most important of which, of course, is to form a conjugating binary solution with ethanol in the appropriate temperature range. The set of criteria established for the selection of the extractant were:

1. The extractant-ethanol mixture should form a conjugating binary solution with an upper critical solution temperature, UCST.
2. The UCST should be in the range 60 to 100°C. The extraction process will take place about 15°C higher than the UCST. The higher the UCST, the higher the source temperature and therefore the cost of energy required by the proposed scheme. This temperature must not be too low, or else insufficient separation between the conjugate solutions will occur at the heat sink temperature.
3. The extractant should be as insoluble in water as possible.
4. There should be a significant density difference between the extractant and ethanol to make the separation easier.
5. The extractant should not corrosively attack the common construction materials.
6. The extractant should exhibit chemical stability, over the system life, under the working conditions.
7. The extractant should not interfere with the use of the alcohol as a fuel.
8. The extractant should not be toxic to the fermentation microorganisms.
9. The extractant should not contaminate the stillage as an animal feed
10. The extractant should not be too expensive and should be easily available.

2.2 Candidate Extractants From the Literature

Although the criteria were useful for identifying the most promising binaries given experimental data, the criteria were not useful for predicting the existence of binaries. Indeed, there is, at present, no generally applicable thermodynamic theory or even correlation which can predict the existence or properties of conjugating binary liquid mixtures. The search for a suitable extractant proceeded, therefore, by screening known conjugating binaries for which some data existed -- typically only the upper critical solution temperature (UCST).

Readily available literature sources containing data on UCSTs for binary mixtures were surveyed to determine candidate extractants. While some of these sources, identified below, had been quickly surveyed before, a more extensive effort was made to identify potential candidate extractants on the basis of data for related compounds; for example, methanol and propanol. Several new compounds were identified in this fashion and, in addition, several new sources of data were identified.

Major literature sources that were surveyed in the course of this project include: (i) A.W. Francis, "Critical Solution Temperatures," Advances in Chemistry Series, Number 31, American Chemical Society 1961; (ii) Sorenson and Arlt, "Liquid-Liquid Equilibrium Data Collection: Binary Systems," Volume V, Part 1, DECHEMA, 1979; and (iii) Chemical Abstracts. Two volumes of the DECHEMA Series; Sorenson and Arlt, "Liquid-Liquid Equilibrium Data Collection," Volume V, Parts 2 and 3, "Ternary and Quaternary Systems," DECHEMA, 1980, that have recently been published on ternary systems could not be procured in time.

Ethanol apparently forms conjugating binary solutions with UCSTs with a wide variety of organic compounds. Most of these compounds are not suitable, however. A list of candidate extractants identified in this initial literature search is outlined in Table 1.

It can be seen from Table 1 that ethanol tends to form conjugating binary solutions with high-molecular-weight aliphatic compounds. The first three or four compounds in Table 1 are in the diesel fuel range. Vegetable oils constitute a number of conjugating binaries with ethanol, and one of these compounds may well be an attractive candidate, depending upon availability. However, many properties of these oils, especially their solubility properties with ethanol and water, are very similar. It does not appear useful nor necessary therefore to test all possible vegetable oils, especially the more expensive ones. Data were found in the literature on the composition of these oils, and the more common oils and representative compositions were selected to be tested. A list of vegetable oils and their properties is shown in Table 2. The compositions of these oils are shown in Table 3.

On the basis of a few solubility data in the literature and data on related systems (i.e., systems of other alcohols and organic solvents) a number of speculative candidate extractants were identified under numbers 13 to 22 in Table 1. No information is available in the literature on whether these solvents form conjugating binaries with ethanol, but on the basis of related data, these solvents appeared to be worth investigating. The first experiment to screen them was to determine whether they have this property or not. Because the densities of anisole and anethole are close to that of water, these may well not be practical solvents for the proposed scheme.

Based on initial laboratory tests, literature survey and the UCST data presented in Table 2, it became clear that a very small amount of impurities in either ethanol or the extractant can cause a significant modification of the phase diagram. For example, the UCST of corn oil or cottonseed oil and ethanol increases from 65°C to 90°C if the moisture concentration in the alcohol increases from 0.1 to 4.6 weight percent (2). Similarly, the UCST of hydrocarbons, and alcohol also very strongly depend upon the particular alcohol. For example, the UCST of cyclohexane-methanol is 46°C and that for cyclohexane-ethanol is -16°C (3). In view of these considerations, the bulk of the experimental work was carried out with absolute alcohol: 199- to 200-proof purity. Denatured alcohol and grain

alcohol, 190-proof, were used only for preliminary screening. Based on initial testing of about 40 different compounds, it was found that:

- Corn oil, boiled linseed oil, mineral oil, cottonseed oil, phenyl ether, decalin and 2,2,4 trimethyl pentane, n-heptane, n-octane and cyclohexane exhibit partial miscibility with denatured alcohol at room temperature, while
- castor oil, anisole, benzaldehyde, methylene chloride, ethylene glycol, propylene glycol, glycerin, dimethyl ether and diethyl ether are completely miscible in denatured alcohol.

Consequently, the bulk of the experimental work concentrated on higher paraffins, vegetable oils and the paraffin oil. The UCST of these extractants with absolute alcohol are presented in Table 4. Because corn oil and cottonseed oil are quite similar in composition and characteristics and because of the availability of the literature data on binary and ternary phase diagram for cottonseed oil-ethanol-water, it was decided to just concentrate on cottonseed oil and drop corn oil. Secondly, since the UCST of tetradecane-ethanol was only about 35°C, it was decided not to consider it any further because this extractant would require refrigeration to accomplish decent separation between the conjugate solutions.

In summary, based on literature search and preliminary screening the list of possible extractants was reduced to the following three compounds:

Hexadecane $C_{16} H_{34}$,
Cottonseed oil, and
Paraffin white light oil.

All of these compounds exhibited conjugate behavior with ethanol. Therefore, a series of experiments was planned to investigate the characteristics of these compounds for their ability to separate ethanol-water mixtures using the proposed scheme.

3.0 DETERMINATION OF BINARY AND TERNARY PHASE DATA

To briefly review, the alcohol extraction step in the proposed scheme occurs at about 100°C (above the upper critical solution temperature UCST), while the alcohol-extractant separation step occurs at about 30°C. The UCST for the binary mixtures of the three extractants of interest with absolute alcohol are presented below.

<u>Extractant (composition)</u>	<u>UCST °C</u>
Hexadecane (50% mole)	49.1
Cottonseed Oil (50% weight)	63.5
Paraffin White Light Oil (50% weight)	102.5

Thus, based on UCST, it is evident that hexadecane is superior because the thermal energy source temperature required for this extractant will be the lowest of the three. However, in order to make the process efficient, it is necessary to select that extractant which has a more complete separation of alcohol and extractant in the two conjugate phases at about 30°C. Consequently, two experimental tests were conducted to estimate the conjugate phase compositions of the three binaries at room temperature using these extractants and ethanol. These tests are described below.

1. Test 1. Determination of Binary Phase Compositions Using Conjugate Solutions

Experiments were conducted to determine the binary phase compositions using conjugate solutions. In these experiments, typically about 2 gm of absolute alcohol and 2 gm of extractant were mixed in a test tube closed from top for about two hours. Then the mixture was left overnight for the two clear conjugate phases to form. Next day samples were withdrawn by means of a syringe from the top phase and then from the bottom phase. Known quantities of these samples were heated in a water bath at 85°C to evaporate alcohol, till a constant weight solution (extractant) was left in the test tubes. This weight was assumed to be the weight of extractant in the original sample, while the amount of weight loss was assumed to be that for ethanol.

The results of these experiments are summarized in Table 5. Based upon these experiments it is clear that paraffin oil has the best overall separation characteristics.

2. Test 2. Determination of Binary Phase Compositions Using Pure Compounds

Another set of experiments were conducted to determine the binary phase compositions for alcohol and extractants using pure compounds. In these experiments a known amount (typically about 3 to 4 gm each) of absolute alcohol was added to about six test tubes which were all closed from top by means of septums. Small but varying amounts of extractant were added to these tubes. The test tubes were gently shaken and left undisturbed to see if the solutions in various tubes exhibit one or two phases. By gradually increasing the amount of extractant the exact composition where the binary solution exhibited two phase behavior was identified. Same procedure was followed to determine the composition of the other conjugate phase. In this case small amounts of absolute alcohol were added to test tubes containing pure extractant. The result of these experiments are also presented in Table 5. Once again it is evident that paraffin oil-alcohol shows the best overall separation at room temperature.

While the two experiments described above are different, they both aim to find the same information. The results obtained using the two experimental approaches are not identical but similar. Unfortunately, there are no literature data for these binary mixtures. The only data available are for cottonseed oil and 99.3% pure alcohol, as presented in Figure 3. The literature data values compare quite well with the results of our two experiments. Upon a closer comparison it appears that the correlation of literature data is better with the results of the second experiment which is considered more accurate because in this experiment we can control the quantities of the two compounds quite accurately and there are no sources of error associated with withdrawing samples from the two phases by the use of a syringe.

3.1 Paraffin Oil as the Most Promising Extractant

Based upon the binary phase composition data at room temperature presented in Table 5, it can be qualitatively concluded that: (i) the quality of the product alcohol will be about 95% ethanol by using either paraffin oil or cottonseed oil, and only about 85% using hexadecane, and (ii) percentage of ethanol in the extractant stream going back to the system for recycling will be about 3% for paraffin oil, 7% for hexadecane and about 14% for cottonseed oil. It is necessary that this percentage should be less than 5 to 15% (ethanol concentration in the beer solution) because only then the recycled extractant will be able to extract ethanol from the feed beer solution. From this point of view, cottonseed oil is the worst of the three extractants identified in the last section.

In summary, paraffin oil offers the overall best separation characteristics at room temperature and was further pursued for complete binary and ternary phase data during the course of this study. In addition, paraffin oil has the following attractive features as well:

1. Paraffin oil is in the fuel oil range and therefore a small percentage of this substance in the final product should not hurt the combustion properties of the ethanol. On the other hand, this could be used directly as fuel and will increase the fuel value of the product stream. Typically the combustion value of C₁₂ or C₁₆ paraffins is about a factor of two higher than that for pure ethanol on the weight basis.
2. The presence of about 3 to 4 percent extractant should not pose any regulatory problem because it is presently required to denature pure alcohol anyway with the addition of about 3 to 5 percent of specified compounds such as methanol or gasoline. In a way credit should be given to the proposed process because the extractant automatically renders the product partially or fully denatured depending upon the temperature of operation and therefore the percentage of extractant.
3. A small residual amount of paraffin oil in the weak beer or stillage recycled to the cooker would perhaps not hurt the animals consuming the stillage as part of their feed. However, this issue needs to be investigated further. Another issue which needs to be investigated is to determine if the presence of small amount of paraffin oil in the weak beer has any negative effect on the

fermentation process. It is estimated that the percentage of paraffin oil in the weak beer solution may be one-half percent only.

3.2 Modification of Cottonseed Oil-Ethanol Binary Phase Compositions by Addition of Water

As pointed out earlier the binary phase diagram is profoundly affected by the presence of a small fraction of water in the solution. Experiments using Test 2 were done to determine the mixture compositions at which the two phases appear.

In one set of these tests, cottonseed oil was gradually added by means of a syringe to different ethanol-water mixtures till the ternary solution indicated the presence of two distinct phases. In another set of tests, ethanol-water solution was gradually injected by means of a syringe to cottonseed oil till the mixture exhibited two distinct phases. The results of these experiments are summarized in Table 6.

The results of these tests correlate very well with the published data (2) on ternary phase diagram. The important finding from these tests is that for the oil-rich phase, the percentage of ethanol drops from about 14% to about 6% by presence of approximately 0.3% water only. Similar drop is also expected for the paraffin oil-ethanol system.

3.3 Conjugate Phase Compositions of Cottonseed Oil-Ethanol-Water Ternary Solution

The objective of these tests was to compare our experimental procedure and data with the published data of Magne and Skau (2) on the conjugate phase compositions of Cottonseed oil-Ethanol-Water ternary solution. In this experiment, different known compositions of ternary solutions were mixed by hand (for 15 seconds every 15 minutes) for a period of 8 hours at room temperature. Then these solutions were left overnight for about 16 hours to separate into two distinct conjugate solutions. Samples were withdrawn by means of a syringe first from the top layers and then from

the bottom layers. These samples were then analyzed by means of a water bath, an oven and the Karl-Fischer titrimeter to determine the percentage of oil, ethanol and water. The details of the experimental technique to determine the composition of a ternary mixture are discussed in the Appendix A.

The results of these tests are summarized in Table 7 and Figure 4 and show a very good agreement with the published data. These experiments confirmed that our experimental apparatus is capable of generating accurate data on the conjugate phase composition of ternary solutions.

3.4 Paraffin Oil-Ethanol Binary Phase Diagram

The test setup shown in Figure A-1 in the Appendix was used to determine the UCST of different ethanol-paraffin oil mixtures. The typical sample was about 2 gm, and the test tubes used in these tests had a volume of about 10 ml. For each mixture composition two samples were prepared, and the UCST for each sample was determined 3 or 4 times. The temperature at which the bulk solution became one clear phase was noted as the critical solution temperature. The results of this test are plotted as a binary phase diagram in Figure 5. The alcohol used for these binary tests had a purity of 99.80%; the remaining 0.20% (by weight) was the moisture content.

This test was repeated with different-quality alcohols: one with 99% ethanol and 1% water and the other with 97% ethanol and 3% water. Since the critical solution temperatures rapidly increased with water content, alcohol with higher than 3% water was not tested. Because of high vapor pressures all the tests were limited to 115°C or below.

3.5 Paraffin Oil-Ethanol-Water Ternary Phase Diagram

Laboratory experiments were done to generate ternary phase composition data at room temperature, 30°C and at 115°C. The general approach in all these experiments was the same and these experiments are discussed below:

3.5.1 Ternary Phase Diagram at Room Temperature

The objective of this experiment was to generate conjugate phase composition data for the Paraffin oil-Ethanol-water solution at room temperature. The salient features of this experiment are outlined below:

- Twelve sealed test tubes containing 10 gm of ternary solution each were prepared. These test tubes contained solutions with 4 different bulk compositions.
- The test tubes were rotated end-over-end to ensure thorough mixing for about 28 hours using an electrical motor.
- Then the test tubes were left undisturbed for about 65 hours thereby allowing the ternary solutions to separate into two conjugate ternary phases.
- Two 2.5 gm samples were withdrawn from each of the test tubes by means of a syringe first from the top phase and about one-half hour later from the bottom phase.
- These samples were analyzed to determine the percent composition of oil, ethanol and water using the technique outlined in the Appendix A.

The results of this experiment are summarized in Figure 6. As is evident from this figure, all the tie-lines (straight line joining the compositions of the oil-rich phase and the ethanol-rich phase) pass through the bulk solution composition points thereby confirming the accuracy of the results. Based upon these results, it appears that the separator if operated at about 20°C can produce an ethanol stream containing 95.3% ethanol, 2.7% oil and 2.1% water as the product and an oil stream containing 97.4% oil, 2.6% ethanol and 0.05% water as extractant for recycling to the extraction subsystem.

3.5.2 Ternary Phase Diagram at 30°C

The procedure for this experiment was similar to the one described above, with the following exceptions:

- The test tubes were placed in a constant temperature water bath at 30°C and were shaken by hand for about one-half minute each every 15 minutes, for about 8 hours.

- The test tubes were left undisturbed for about 15 hours, thereby allowing the ternary solutions to separate into two conjugate ternary phases.
- The samples were withdrawn while the test tubes were still in the bath.

The results of this experiment are summarized in Figure 7. Comparison of these data with the corresponding data at 18.4°C shows that the separation of oil and ethanol becomes better if the separator operates at a lower temperature.

3.5.3 Ternary Phase Diagram at 115°C

Since the UCST of the paraffin oil-ethanol binary system is about 105°C, the extraction subsystem in the proposed scheme will operate at a temperature somewhat higher than 105°C. Consequently, it was decided to generate the ternary phase diagram data at 115°C. The procedure for this test was similar to the one described above except that a cooking oil bath was used for heating the ternary solutions and each test tube had only 5 gm of ternary solution. However, because of the high temperature and therefore a high vapor pressure, several difficulties were experienced, including (i) loss of vapors from the septums, (ii) bursting of the septums due to pressure build up, and (iii) loss of ethanol and water vapors when the samples from the upper and lower phases at 115°C were withdrawn and transferred to different test tubes for analysis. The experimental technique was slightly modified to overcome these difficulties; nevertheless the accuracy of these data is somewhat poorer than the ternary phase data at 30°C.

The data for this experiment was generated in five tests over a period of six weeks. Some of the data were also repeated to get the necessary accuracy. The results of these tests are presented in Figure 8 and Table 8. While Table 8 contains all the experimental data, only part of this data are shown in Figure 8. As is evident from Figure 8, several of the tie-lines do not exactly pass through the bulk solution composition points. More seriously, some of the tie-lines actually cross other tie lines. Unfortunately, due to congestion of the tie-lines, it was not possible to generate more accurate data for the oil-rich phase using the present

procedure. A correlation was developed for smoothing out the conjugate phase data and is discussed in Sections 4.3.1. However, the shape of the ternary phase diagram presented in Figure 8, will not change significantly. Based upon data presented in this figure, the following general comments can be made.

1. At low ethanol concentrations, the extractant and water have very low miscibility even at 115°C.
2. As the ethanol concentration in the bulk solution is increased, most of it goes to the water-rich phase rather than the oil-rich phase, indicating that ethanol has much higher affinity for water than oil even at 115°C.
3. In the zone between the tie-lines 1 to 8, Figure 8, the oil-rich phase was on the top and the water-rich phase was at bottom because density of water is higher than that for oil. However, in the zone between tie-lines 9 to 13 the opposite was true, i.e., the ethanol-rich phase was on the top of the oil-rich phase. In the intermediate region, between tie-lines 8 and 9, the two conjugate phases had almost equal density, and consequently the two phases were intermingled and did not form a distinct single interface thereby making the withdrawal of the samples from the two phases almost impossible. For this reason, no reliable data could be generated for this zone. This information will be useful in the design of the extraction subsystem in the proposed scheme.
4. Depending upon the feed and product reflux rates, the maximum concentration of ethanol in the extractant phase will be in the range of 7 to 10%. This stream will be fed to the separator at about 30°C for separation into the ethanol product stream and the "pure" extractant stream for recycling back into the system.

4.0 DESIGN AND ANALYSIS OF THE BASELINE SYSTEM

4.1 Description of the Proposed Baseline System

In the conceptual flow sheet of the proposed scheme, shown in Figure 2, the heated beer feed solution, stream 6, is fed to an extractor along with heated extractant, solution 1. The output from the contactor goes to a separator from which solution 2, a mixture of extractant and ethanol, and water to be recycled to the cooker emanate. If the extractor-separator process is visualized to be a single equilibrium stage, the two output streams are of course in equilibrium with each other and are found at the ends of a connecting tie-line on the phase diagram.

In a single-stage extraction process, the extractant product will be only slightly richer in ethanol than the feed extractant because, based on experimental data presented in the last section, the ratio of the concentration of ethanol in the oil-phase to that in the water phase is small and is much less than 1. For an extract product richer than that possible by a single-stage process, additional stages are required. Even then, with the feed introduced at the end of a multistage process, the extract product can never be richer than the concentration in equilibrium with the feed. To obtain a still richer extract product requires extraction stages above the feed point with product ethanol introduced as reflux, in a manner which is analogous to the design and operation of the enriching section of a distillation column. Even with solute reflux the extract product can have a composition which is no richer than the composition at the plait point in the limit of an ideal process--i.e., a process with an infinite number of stages. The baseline system for the proposed process is presented in Figure 9. The two major differences between the baseline system and the conceptual system presented earlier in Figure 2 are:

- the extractor-separator subsystem is replaced by a continuous column comprising of an enriching and a stripping section. Thus, the single-stage operation has been replaced by a multistage operation.

- A fraction of the ethanol product from the extractant-ethanol separator is recycled back to the extraction subsystem. This in turn improves the quality of the product alcohol from the proposed scheme.

Except for these two differences, the baseline system is similar to the conceptual system which has been described earlier in this report.

4.2 Mass and Energy Balance Equations

To develop the flow sheet for the baseline system using the proposed scheme, a set of mass and energy balance equations was developed. These equations are presented in the Appendix B.

In the formulation of the energy balance, the assumptions were made that there are no heat effects in the extractor-contactor or the phase separator, and any heat transferred is sensible heat only with no phase changes occurring anywhere in the process.

This simple model was used to calculate flow rates and amounts of heat inputs. The model was not used in its entirety in a formal way, but rather to calculate the mass balances around individual units.

4.3 Design of the Separator and Extraction Subsystems

The designs of the separator and extraction subsystems are coupled because of the two recycle streams--the ethanol reflux and the recycled extractant. The two designs can be uncoupled and the analysis can proceed by making certain assumptions and setting specifications on product compositions. The initial assumption concerns the composition of the extract product. The material balance around the separator can then be determined, and finally, with the reflux composition fixed, the extractor can be designed.

4.3.1 Smoothed Equilibrium Line

Although the phase equilibrium data at 115°C were plotted on a ternary phase equilibrium diagram, it was found to be more convenient for

design calculations to replot the data as a x (concentration of ethanol in the water phase) - y (concentration of ethanol in the oil phase) diagram. To smooth the data, particularly in the region of low ethanol content, and develop a more consistent equilibrium line, the data on x and y were first plotted versus the independent variable controlling the compositions--the weight fraction of ethanol in the bulk solution, which was determined accurately in making up the solution (the oil fraction was kept constant).

Figures B-1 and B-2 show these correlations of conjugate phase composition data with concentration of ethanol in the bulk solution. As Figure B-1 shows, the data on concentration of ethanol in the water phase were fairly consistent. However, the data on concentration of ethanol in the oil phase showed considerable scatter at low concentrations and this correlation was very useful in smoothing the data.

An equilibrium x-y diagram was developed by selecting pairs of x and y points from the two correlations and plotting them. This smoothed equilibrium curve is shown in Figure B-3. This curve was used for determining the design of the extractor-contactor.

As a practical limit the maximum concentration of ethanol in the extract product was chosen to be 8.5%. The corresponding equilibrium concentration of ethanol in the water phase is 47.5%. This pair of equilibrium concentrations is found at a bulk concentration of ethanol (in the experiments to determine the phase equilibrium diagram) of 30% (and 50% paraffin oil), as may be seen in Figures B-1 and B-2.

The extract product was therefore specified as containing 8.5% ethanol. On the ternary phase equilibrium diagram in Figure 8, this product also is found to contain about 91% paraffin oil and 0.5% water.

4.3.2 Composition of the Extract Product

Even with the use of ethanol product as reflux to obtain a higher concentration of ethanol in the extract product, various types of constraints

can operate to limit this concentration in a practical application. In the present case, for example, an isopycnic tie-line was found in the region of a bulk concentration of 32-38% ethanol and 50% paraffin oil. For this type of tie line, the conjugate solutions have the same density, and the two phases do not settle into separate layers. In any extraction process it is not possible to continue the process beyond an isopycnic tie-line.

4.3.3 Material Balance Around Separator

The extract product is of course cooled to about 30°C to separate an ethanol-rich product from an oil-rich extractant phase which is then recycled. To determine the compositions of the two separated phases by interpolation, the equilibrium phase data obtained at 30°C (Figure 7) were plotted versus the independent variable controlling the compositions--the weight fraction of water in the bulk solution (the oil fraction was kept constant at 50%).

Figures B-4 and B-5 show these correlations of conjugate phase composition data with concentration of water in the bulk solution. With a bulk solution concentration of water of 0.5%, the ethanol-rich phase contains about 4.5% oil and 0.8% water, the ethanol concentration by difference being then 94.7%. The extractant phase contains 96.5% oil and essentially no water, the concentration of ethanol then being 3.5%.

It should be possible to solve material balance equations, knowing the two conjugate phase compositions and the bulk solution composition, to obtain the relative amounts of the two conjugate solutions obtained upon cooling the bulk solution. However, the conjugate solution compositions, being obtained experimentally, contain some imprecision so that they do not satisfy all of the necessary material balance constraints. In addition the experimental data must be interpolated for the conditions of interest.

Material balances for ethanol and oil were used to determine the amounts of the two conjugate phases. The total material balance was then

satisfied by normalizing the amounts found (the sum of which did not equal the total mass in the bulk composition) to the total mass. The extract product, upon being cooled was found to split into the ethanol-rich product and the extractant to be recycled in the ratio of 1:17.08.

Because the extractant to be recycled contains 3.5% ethanol, the feed to the extractor-contactor must have an ethanol content higher than the concentrating in equilibrium with this amount. (Otherwise ethanol will not be transferred from the water to the oil phase.) The lower limit on feed ethanol content for this process is therefore 15% ethanol, as may be seen from Figure B-3. Furthermore, 15% ethanol is the lower limit on the raffinate product as well.

4.3.4 Design of the Extraction Subsystem

The extraction subsystem was designed by means of standard procedures(5). Because the phase equilibrium cannot be expressed algebraically the calculation of number of stages and amount of extractant required was done graphically on the phase diagram. The design of the extraction subsystem was determined on the basis of the ternary phase equilibrium diagram at the extraction temperature of 115⁰C. Although it is possible to use the ternary phase diagram itself for the graphical calculations of the number of stages, it was easier to use the smoothed equilibrium curve on the x-y diagram, which was described above in Section 4.3.1.

For each case considered an operating line, which is derived from a material balance around each stage and the end of column, and relates the compositions of the two phases at each point within the column, was drawn on the graph with the equilibrium line, separate lines being drawn for the sections above and below the feed stage. The stages were then stepped off between the lines. A design of the extractor-contactor was determined for each of a number of combinations of reflux ratio and concentration of ethanol in the feed.

As indicated in the discussion above on the operation of the separator, the amount of ethanol in the recycled extractant causes the concentration of ethanol in the raffinate product to be limited to a value no lower than 15%. As a practical limit the ethanol content of the raffinate product was taken to be 16.5% for all cases.

4.4 Performance of the System

For each design of the extractor-contacter, the mass balance equations were solved for relative flow rates. (For each case the design of the separator remained constant because the concentration of the extract product was taken as a given value.) The results of the extractor design calculations and the material balance calculations are shown in Table 9. The physical properties of ethanol, water and paraffin oil over the desired temperature range are outlined in Table B-1 in the Appendix B. The effectiveness of the different heat exchangers was assumed to be 0.8.

Table 9 shows results as a function of reflux ratio and feed ethanol concentration. The higher the reflux ratio the lower will be the limit on the feed ethanol concentration which can be treated by the system. However, the higher the reflux ratio, also the lower will be the ethanol product rate. At a constant feed ethanol concentration it is better to use a lower reflux ratio, which gives a higher product rate (at the expense of an extractor-contacter with a greater number of stages). For the cases considered the number of stages in the extractor-contacter is not excessive.

Table 10 shows the results of the energy balance calculations. The largest single heater input is that required to heat the recycled extractant before it goes into the extractor-contacter.

The ratio of heat input to product fuel value is a strong function of reflux ratio, which of course determines the product rate for a constant flow of extractant. For a reflux ratio of less than 0.03, this ratio is less than 0.073 i.e., less than 7.3% of the product fuel value is used as the

thermal energy input for the proposed separation system. Of course, for these conditions this separation process can be used only with feeds containing more than 23% ethanol. As the ethanol product from this process does contain a few percent (4.5%) of paraffin oil, some of the product fuel value (7.1%) is contributed by the residual oil in the product streams.

However, the product does contain almost no water (less than 1%), and is suitable for use as a fuel as it is produced from the process.

4.5 Description of Extractor-Contactor Column

A wide variety of extraction equipment is available for countercurrent contacting of two essentially immiscible liquid phases. Such equipment includes devices that create interfacial contacting area solely by liquid head or jets (e.g., plate and spray columns) and other devices that incorporate mechanical agitation (e.g., pulsed, rotating disk, and reciprocating plate columns). Because mass transfer rates for liquid-liquid contacting are greatly increased when mechanical agitation is provided, the latter devices are the ones most commonly used. A popular device for liquid-liquid extraction is the rotating-disc contactor (RDC), which offers ease of design, construction, and maintenance; provides flexibility of operation; and has been thoroughly tested on a commercial scale. The RDC has been constructed in diameters up to at least 9 ft and is claimed to be suitable for diameters up to 20 ft.

Table B-2 in the Appendix B lists the advantages and disadvantages of a number of types of contactors. The simple spray column tends to have a low efficiency because of the back mixing which can occur. Plate and packed columns probably should not be used for the present application because of the possibility of fouling from the solids contained in the beer solution. A centrifugal extractor or a mixer-settler system has high efficiency but at the cost of a significant power consumption. The rotating-disc contactor is probably a good compromise choice of type of equipment for the present application.

Because of the larger number of important variables, estimation of column diameter for liquid-liquid contacting devices can be far more complex and is more uncertain than for the vapor-liquid contactors. These variables include individual phase flow rates, density difference between the two phases, interfacial tension, direction of mass transfer, viscosity and density of the continuous phase, rotating speed and compartment geometry. Column diameter is best determined by scale-up from tests run in standard laboratory or pilot plant test units, which have a diameter of 1 in. or larger.

However, for the conceptual process design for the present application, a method in the recent literature (6) was used to estimate the size of a suitable rotating-disc contactor. The case of a feed with 30% ethanol was chosen as a base case. A reflux ratio of 0.03 was selected, and the relative flow rates and equilibrium extraction stages required are shown in Table 9.

This plant is assumed to produce 5 million gallons of ethanol product a year, operating with an on-stream factor of 90%. The product flow rate is then 31.8 kg/min (4,200 lb/hr) and the extract product flow rate is 1,250 kg/min (165,400 lb/hr). The feed rate is 176.5 kg/min (23,300 lb/hr) of 30% ethanol solution.

For the 11 theoretical stages required in the extractor-contactor, a column 7 m (22 feet) high is required. To handle the plant capacity, 10 columns are needed, each with a diameter of 3.7 m (12 feet).

4.6 CONCLUSIONS

Based upon the preliminary analysis presented in this section the following conclusions can be drawn:

1. The proposed ethanol-water separation scheme using partially miscible conjugating liquid system should work.

2. The proposed scheme using paraffin white light oil as extractant at 115°C and separation of ethanol product and the recycled extractant at 30°C should produce the final product with 94.7% ethanol, 4.5% oil and 0.8% water by weight. Since paraffin oil is in the fuel oil range and has a combustion value about twice that for ethanol, the final product can be directly used as motor grade fuel. Secondly, the presence of 4.5% oil should not pose any regulatory problem because it is presently required to denature pure alcohol anyway with the addition of about 4 to 5% of specified compounds such as methanol or gasoline.
3. Depending upon the reflux ratio and the ethanol concentration in the feed the thermal energy required by the proposed system will vary between 4 to 34% of the fuel value of the final product. For the baseline system of 5 million gallons per year capacity with an ethanol feed concentration of 30% the thermal energy required by the proposed scheme will be about 7.3% of the fuel value of the product.
4. The overall design of the proposed scheme should be simpler than the conventional distillation system producing the same quality product. The three heaters, one cooler and the two heat exchangers required for the proposed system should be relatively inexpensive, not only because there is no phase change (i.e., evaporation and condensation as in a conventional distillation system), but also because the operating temperatures and pressures are quite modest. Simple, inexpensive plate heat exchangers developed for geothermal and ocean thermal energy conversion should be usable in the proposed scheme. Typically these heat exchangers are estimated to cost one-half to one-quarter of the conventional shell and tube heat exchangers.
5. There is quite an uncertainty in the sizing of the extraction subsystem because it depends upon a number of variables including the individual phase flow rates, density and viscosity of the two phases, interfacial tension and the geometry of the column. Because of a lack of performance data it is recommended that the standard laboratory tests should be undertaken. The data from these tests can then be used to estimate the exact sizing of the extraction subsystem.
6. While the design of the separator will be relatively simple, however, laboratory experiments are recommended to determine the minimum residence time for different geometries and flow velocities. One such design is outlined in Figure B-6 in the Appendix B.

5.0 REFERENCES

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Table 1. Possible Extractants and Their Properties

Compound	Formula	Molecular Weight	Upper Critical Solution Temperature, °C	Density g/ml	Melting Point, °C	Normal Boiling Point, °C
1. n-Tetradecane	$C_{14}H_{30}$	198.4	31	0.765	5.5	252
2. n-Hexadecane	$C_{16}H_{34}$	226.4	55	0.775	18 to 20	288
3. 2, 13-Dimethyl tetradecane			38.7			
4. 1-Octadecene	$C_{18}H_{36}$	252.5	47	0.791	18	179
5. Turpentine			108.2			
6. Corn Oil			65	0.92-0.93	-10 to -20	
7. Cottonseed Oil			60	0.917	12 to -13	
8. Peanut Oil			65	0.92-0.93	3	
9. Sesame Oil			62	0.92	-4 to -6	
10. Soybean Oil			65	0.92-0.93	-10 to -16	
11. Boiled Linseed Oil			60	0.93-0.94	-19 to -27	
12. Paraffin Oils*			33-128			
13. Methylene Chloride	CH_2Cl_2	84.9		1.33	-96.7	40
14. Decalin (trans, cis)	$C_{10}H_{18}$	138.2		0.870, 0.896	-31.5, -43.3	185, 195

* A class of oils including light and heavy paraffin oils, mineral oils, Nujol, etc.

Table 1. Possible Extractants and Their Properties (Continued)

Compound	Formula	Molecular Weight	Upper Critical Solution Temperature, °C	Density g/ml	Melting Point, °C	Normal Boiling Point, °C
15. Anisole (methoxy benzene)	C_7H_8O	108.2		0.996	-37.5	155
16. Anethole (1-methoxy, 4-propenyl benzene)	$C_{10}H_{12}O$	148.2		0.988	21.4	234.5
17. Benzaldehyde	C_7H_6O	106.1		1.042	-26	178.1
18. Benzl ethyl ether	$C_9H_{12}O$	136.2		0.949		185
19. Phenetole (ethoxy benzene)	$C_8H_{10}O$	122.2		0.967	-29.5	170
20. Phenyl ether	$C_{12}H_{10}O$	170.2		1.075	26.8	257.9
21. Ethylene chloride	CH_2ClCH_2Cl	99.0		1.257	-35.3	83.5
22. Pinacolyl alcohol	$(CH_3)_3CCHOHCH_3$	102.2		0.812	5.5	121

Table 2. Literature Data on Vegetable Oils

Oil	Acid Value	Iodine Value (Wijs)	Saponification Value	Critical Solution Temperature with Aqueous Ethanol, °C		
				99.9 Weight % Ethanol	98.0	95.4
Soybean	1.029	129.6	192.2	65	75	90
Cottonseed	4.56	105.6	194.6	65	70	90
Peanut	2.723	94.62	191.9	70	80	95
Sesame	2.5	112.7	191.4	65	75	90
Corn	1.52	120.2	189.7	65	75	90
Linseed	1.48	182.5	191.3	60	70	80

Source: Reference 4.

Table 3. Compositions of Vegetable Oils

Oil	Constituent Fatty Acids, g/100g Total Fatty Acids									
	Saturated					Unsaturated				
	Lauric C12:0*	Myristic C14:0	Palmitic C16:0	Stearic C18:0	Arachidic C20:0	Palmitoleic C16:1	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Other
Castor	2.4						7.4	3.1		87**
Corn		1.4	10.2	3.0		1.5	49.6	34.3		
Cottonseed		1.4	23.4	1.1	1.3	2.0	22.9	47.8		
Linseed			6.3	2.5	0.5		19.0	24.1	47.4	0.2
Peanut			8.3	3.1	2.4		56.0	26.0		3.1, 1.1
Sesame			9.1	4.3	0.8		45.4	40.0		
Soybean	0.2	0.1	9.8	2.4	0.9	0.4	28.9	50.7	6.5	0.1

* Shorthand notation for number of carbon atoms; number of unsaturated double bonds.

** Ricinoleic, C18:1 (12-OH).

Source: "Handbook of Chemistry and Physics", Chemical Rubber Publishing Company, 36th Edition, 1954.

**Table 4. Upper Critical Solution Temperature of Candidate
Extractants with Absolute Alcohol**

<u>Extractant (Extractant Concentration)</u>	<u>Upper Critical Solution Temperature, °C</u>	
	<u>Experimental*</u> <u>Value</u>	<u>Literature Data</u>
Tetradecane (50% Mole)	35.7	31
Hexadecane (50% Mole)	49.1	55
Corn Oil (60% Weight)	65.5	65
Cottonseed Oil		
(60% Weight)	60.3	65
(50% Weight)	63.2, 64.0	
Paraffin White Light Oil		
(60% Weight)	101.6, 104.5	33-128
(50% Weight)	101.8, 102.8	
Paraffin White Heavy Oil		
(60% Weight)	more than 118	33-128

* Quality of Alcohol = 99.95% Ethanol.

Table 5. Binary Data on Conjugate Solutions: Ethanol-Extractant
(Ethanol had 0.046% water)

<u>Extractant</u>	<u>Temperature</u> °C	<u>Ethanol Concentration in Two Phases, Weight Percent</u>		<u>Reference</u>
		<u>Ethanol Rich</u>	<u>Extractant Rich</u>	
Cottonseed Oil	16.2	93.4	14.5	Test 1**
	19.0	95.9	14.0	Test 2
		97.3	8.2	Literature*
Paraffin Oil	19.4	93.6	5.5	Test 1
	19.0	96.8	1.9	Test 2
Hexadecane	19.2	85.6	7.5	Test 1
	19.0	83.4	5.6	Test 2

* F.C. Magne and E.L. Skau, J. Amer. Oil Chem. Soc., 30, 288-291 (1953).
See also Figure 3. This data is with 99.3% Ethanol.

** The data for Test 1 are average of 3 to 4 samples.

**Table 6. Equilibrium Composition of Ternary Solutions:
Ethanol-Cottonseed Oil-Water**

<u>Mixture</u>	<u>Temperature</u>	<u>Weight Percent</u>			
		<u>Ethanol</u>	<u>Oil</u>	<u>Water</u>	
Binary	19.0	95.9	4.1	0	
Ternary	19.2	86.1	0.3	13.6	Ethanol Rich Phase
		85.1	0.6	14.3	
		85.8	0.4	13.7	
		89.4	0.3	10.3	
		88.4	0.8	10.8	
		89.5	0.6	9.9	
		93.1	1.0	5.9	
		93.25	0.8	5.95	
		93.1	0.6	6.3	
		95.8	1.3	2.9	
		96.0	2.0	2.0	
		96.1	1.4	2.5	
Binary	19.0	14.0	86.0	0	
Ternary	19.2	6.64	93.02	0.33	Oil Rich Phase
		5.80	93.91	0.29	
		5.18	94.56	0.26	

Note: The binary data is taken from Table 5.

Table 7. Comparison of the Experimental Data With the Published Data on Conjugate Phase Composition of Cottonseed Oil - Ethanol - Water Mixture

Reference	Temp °C	Original Overall Composition			Composition of Oil-Rich Phase			Composition of Ethanol-Rich Phase		
		O	E	W	O	E	W	O	E	W
(2)	30	47.45	47.68	4.87	92.45	7.12	0.43	1.09	88.53	10.38
New Data	21.2	47.21	47.54	5.25	92.18	7.53	0.29	0.83	89.83	9.34
	21.2	47.21	47.54	5.25	93.03	6.68	0.29	1.40	89.26	9.34
	19.0	47.33	47.66	5.0	95.3	4.53	0.17	0.75	88.59	10.66
	19.0	47.33	47.66	5.0	94.3	5.53	0.17	----	----	----
(2)	30	49.47	42.99	7.54	93.55	6.03	0.42	0.58	83.74	15.68
New Data	21.2	49.34	42.95	7.71	94.44	5.27	0.29	0.85	85.65	13.50
	21.2	49.34	42.95	7.71	94.27	5.44	0.29	0.47	86.03	13.50
	19.0	49.33	42.66	8.0	94.7	5.13	0.17	0.46	83.91	15.63
	19.0	49.33	42.66	8.0	93.2	6.63	0.17	0.53	83.84	15.63

O: Oil; E: Ethanol; W: Water

All entries are weight percent.

Table 8. Conjugate Phase Data For Ethanol-Water Paraffin Oil Ternary Solution at 115°C

Water/Ethanol-Rich Phase			Oil-Rich Phase			Bulk Solution			Reference
O	W	E	O	W	E	O	W	E	
1.68	95.41	2.91	98.32	0.13	1.55	50.0	48.0	2.0	5
1.62	92.65	5.72	98.20	0.12	1.68	50.0	46.0	4.0	5
0.40	92.26	7.34	95.78	0.41	3.81	50.0	45.0	5.0	1
1.19	87.04	11.77	94.81	0.13	5.06	50.0	42.0	8.0	5
0.61	78.13	21.26	97.52	0.21	2.36	50.0	40.0	10.0	4
1.64	86.98	11.38	96.41	0.28	3.31	50.0	40.0	10.0	1
2.18	81.33	16.50	94.18	0.40	5.42	50.0	38.0	12.0	5
0.18	77.60	22.22	97.29	0.11	2.60	50.0	35.0	15.0	2
0.20	71.36	28.44	96.88	0.12	3.00	50.0	30.0	20.0	2
0.33	59.22	40.45	97.49	0.20	2.31	50.0	30.0	20.0	4
2.34	53.14	44.52	92.36	0.47	7.16	50.0	25.0	25.0	5
0.59	62.55	36.86	96.40	0.08	3.51	50.0	25.0	25.0	2
0.44	58.46	41.10	96.53	0.07	3.40	50.0	20.0	30.0	2
2.42	45.96	51.62	--	--	--	50.0	20.0	30.0	4
1.72	18.26	80.02	--	--	--	50.0	10.0	40.0	4
1.94	22.33	75.73	88.60	0.70	10.70	50.0	10.0	40.0	3
3.82	14.42	81.76	87.27	0.70	12.03	50.0	6.0	44.0	3
3.67	7.51	88.82	79.15	0.45	20.40	50.0	4.0	46.0	4
8.16	3.57	88.27	80.57	0.22	19.21	50.0	2.0	48.0	4
11.77	2.01	86.23	81.11	0.13	18.75	50.0	1.0	49.0	4

Reference: This data was generated in 5 batches as follows:

1. 20 April
2. 27 April
3. 4 May
4. 14 May
5. 20 May

O: Oil W: Water E: Ethanol
 All entries are weight percent

Table 9. Design of Extractor-Contactor and Material Balances as Function of Reflux Ratio

Reflux Ratio = Reflux/ Extract Product	Lower Limit Feed Conc. Wt. Frac. ETOH	ETOH Conc. in Feed Wt. Fraction	No. of Stages		Material Balance around ¹ Extractor-Contactor Extract Product = 100			Material Balance ^{1,4} around Separator Extract Product = 100		
					Reflux	Feed	Raffinate ³ Product	Extractant into Extractor	ETOH Product	Makeup ² Extractant
0.05	0.175	0.20	2	3	5	9.27	8.38	94.11	0.53	0.07
		0.25	1	3	5	3.72	2.80	94.08	0.53	0.04
		0.30	1	3	5	2.38	1.45	94.07	0.53	0.03
		0.35	1	3	5	1.70	0.77	94.07	0.53	0.03
		0.40	1	3	5	1.36	0.43	94.07	0.53	0.03
0.04	0.23	0.25	2	6	4	13.06	11.23	94.17	1.53	0.12
		0.30	1	5	4	8.23	6.38	94.15	1.53	0.10
		0.35	1	4	4	5.98	4.11	94.13	1.53	0.09
		0.40	1	4	4	4.72	2.85	94.13	1.53	0.08
0.03	0.28	0.30	2	9	3	14.10	11.32	94.22	2.53	0.17
		0.35	1	6	3	10.24	7.44	94.20	2.53	0.15
		0.40	1	5	3	8.08	5.27	94.19	2.53	0.14
		0.45	1	4	3	6.64	3.82	94.18	2.53	0.13
0.02	0.34	0.36	4	14	2	13.81	10.07	94.26	3.53	0.21
		0.40	2	11	2	11.44	7.69	94.25	3.53	0.20
		0.45	1	8	2	9.41	5.65	94.24	3.53	0.19
0.01	0.40	0.42	3	14	1	13.65	8.95	94.30	4.53	0.25
		0.45	1	11	1	12.18	7.47	94.29	4.53	0.24

¹There are minor discrepancies between the material balances for the extractor-contactor and the separator because there are inaccuracies in the assumed split in the separator due to experimental error in the compositions of the two streams leaving the separation.

²Makeup extractant was calculated as the sum of the extractant (4.5% by weight) in the ethanol product and the extractant (0.5% by weight) in the raffinate product, i.e., by means of a balance for paraffin oil taken over the entire system.

³Raffinate product is assumed to contain 16.5% ethanol by weight.

⁴Total ethanol product from separator = 5.53 and extractant stream recycled = 94.47 for all cases.

Table 10. Energy Requirements as Function of Reflux Ratio

Reflux Ratio = Reflux/ Extract Product	ETOH Conc. in Feed Wt. Fraction	Heat Supplied by Heaters Calories		Total Heat* Input In Heaters 1,2&3 Calories	Product ¹ Fuel Value Calories	Ratio of Heat Input to Product Fuel Value
		1 ⁺	2			
0.05	0.20	182	248	1,300	3,830	0.339
	0.25		248		3,830	
	0.30		248		3,830	
	0.35		248		3,830	
	0.40	65	248		1,183	
0.04	0.25	268	200	1,338	11,060	0.121
	0.30		200		11,060	
	0.35		200		11,060	
	0.40	145	200		1,215	
0.03	0.30	313	149	1,332	18,290	0.073
	0.35		149		18,290	
	0.40		149		18,290	
	0.45	204	149		1,223	
0.02	0.36	340	100	1,310	25,520	0.051
	0.40		100		25,520	
	0.45	275	100		1,245	
0.01	0.42	368	50	1,288	32,750	0.039
	0.45	347	50		1,267	

*For all cases the amount of heat exchanged in Heat Exchanger 2 is 3,480 calories, the heat input in Heater 3 is 870 calories, and the heat removed in Cooler 1 is 1,160 calories.

⁺Calculated with the assumption that a heat exchanger (which is 80% effective) is used to recover heat from the raffinate product and heat up the feed.

¹Each gram of product has a fuel value of 7,230 calories; 6,717 (or 92.9%) from the ethanol and approximately 513 (or 7.1%) from the paraffin oil.

FIGURE 1

Example Phase Diagram for Ethanol-Cottonseed Oil Showing Details of the Proposed Extraction Process Using Conjugating Solutions

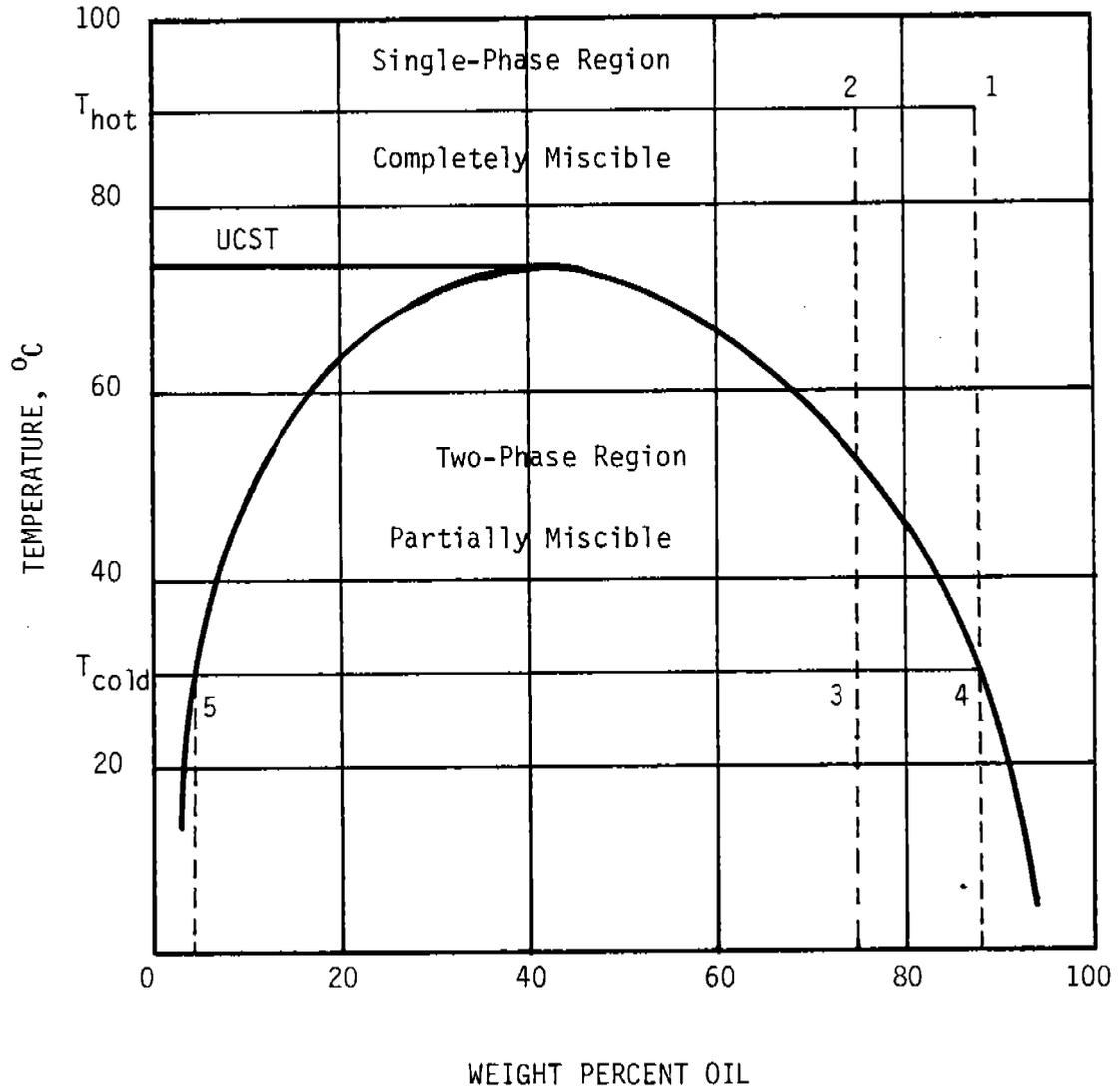


FIGURE 2

Conceptual Diagram of the Proposed Extraction Process Using Conjugating Solutions

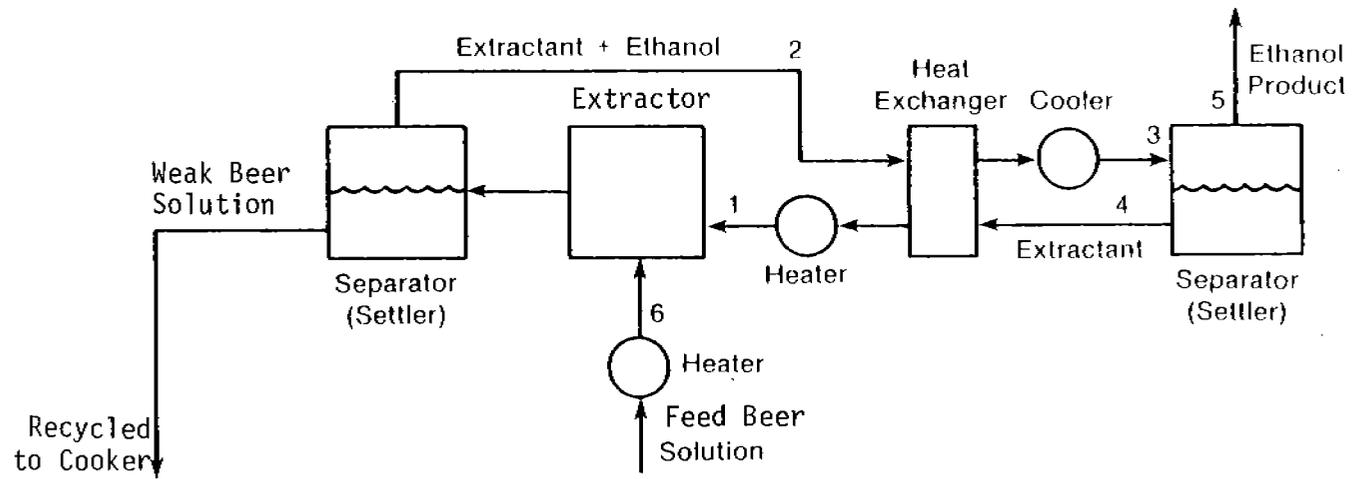
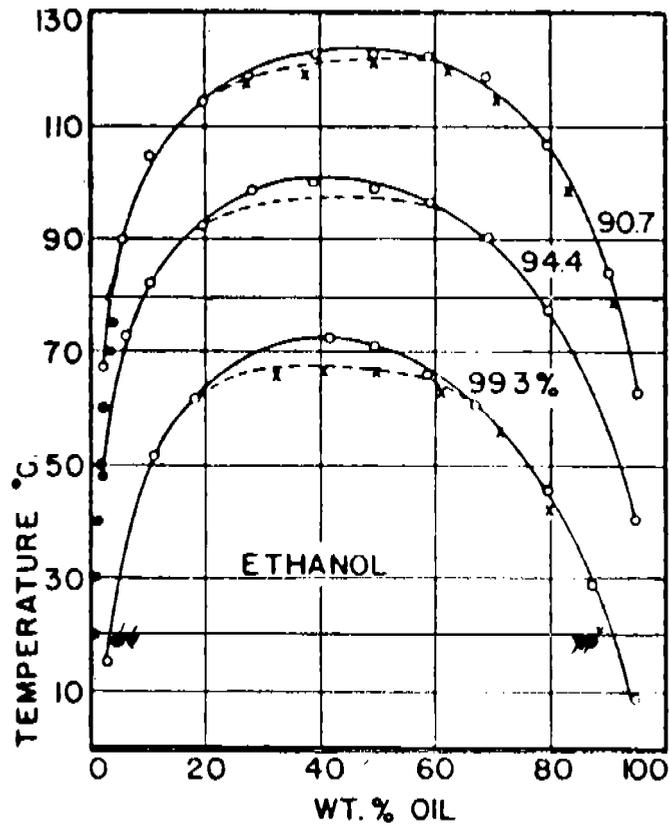


FIGURE 3

Comparison of Ethanol-Cottonseed Oil Binary
Phase Data with the Literature Values



Laboratory tests were made with alcohol containing 99.95% Ethanol

- ▼ Results from Test No. 1
- Results from Test No. 2

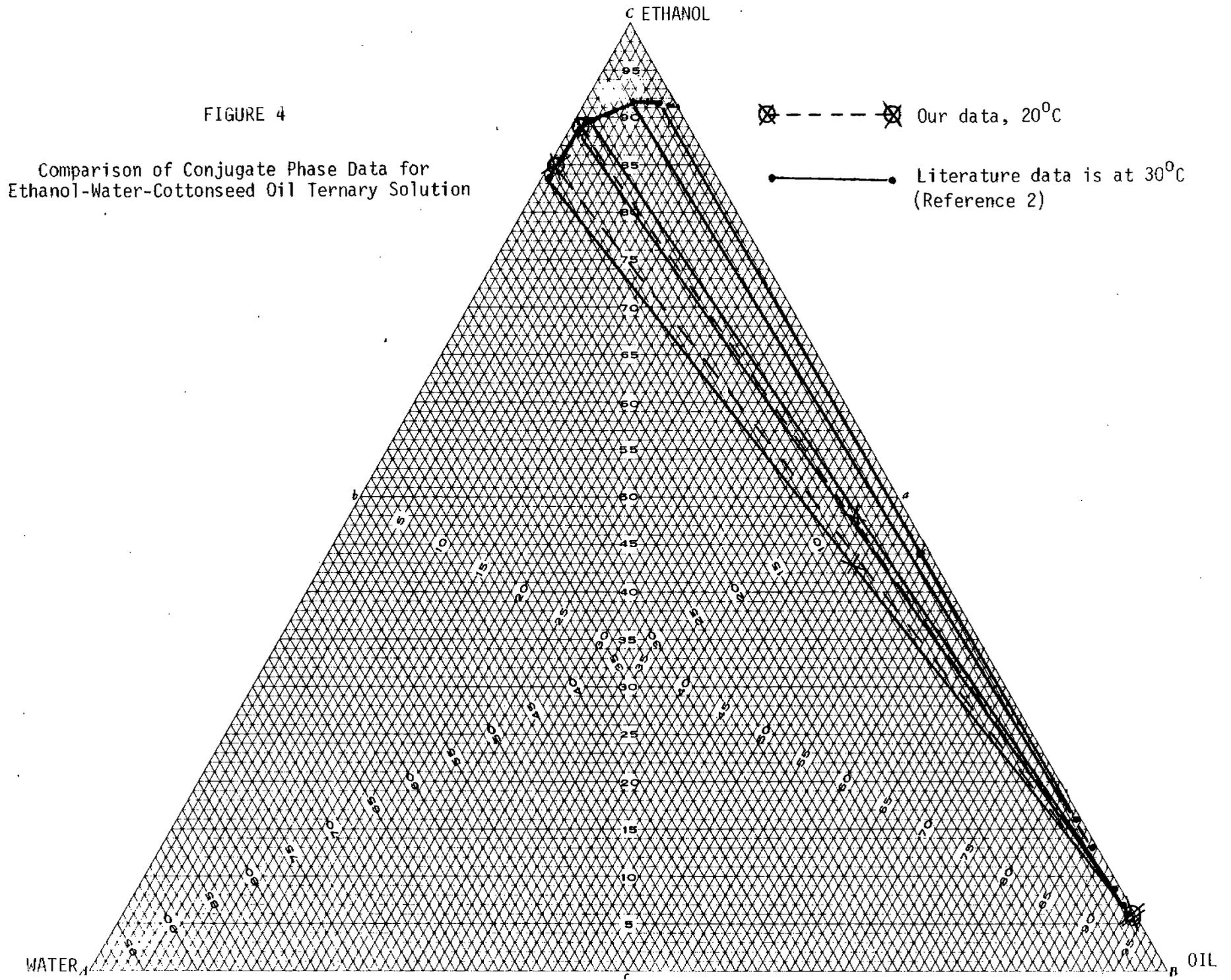


FIGURE 4

Comparison of Conjugate Phase Data for Ethanol-Water-Cottonseed Oil Ternary Solution

⊠ - - - ⊠ Our data, 20°C

● — ● Literature data is at 30°C (Reference 2)

WATER

C ETHANOL

OIL

FIGURE 5

Binary Phase Diagram of Alcohol-Paraffin
Oil with Different Quality Alcohols

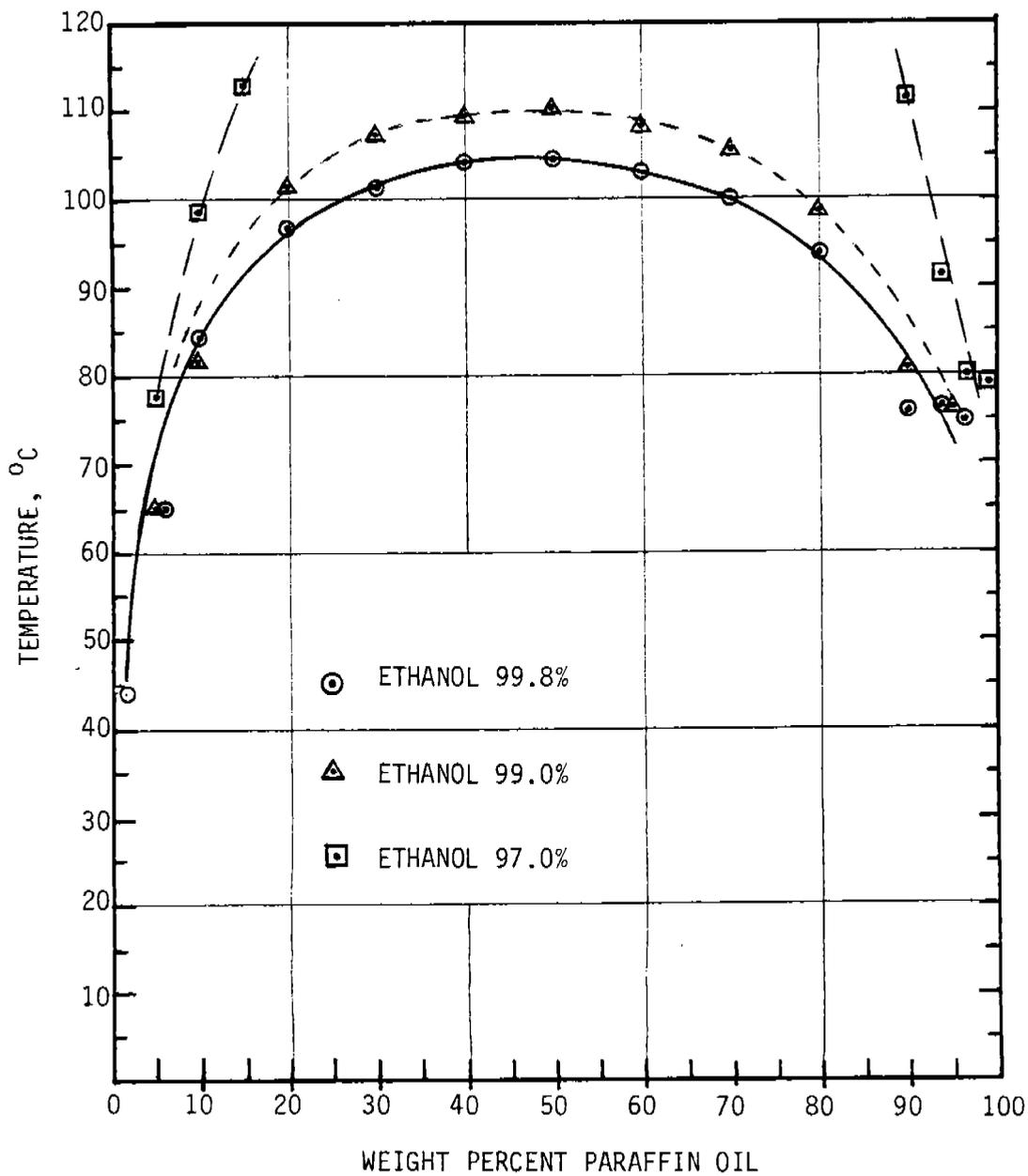


FIGURE 6

Conjugate Phase Data for Ethanol-Water-Paraffin Oil Ternary Solution at Room Temperature (18.4°C)

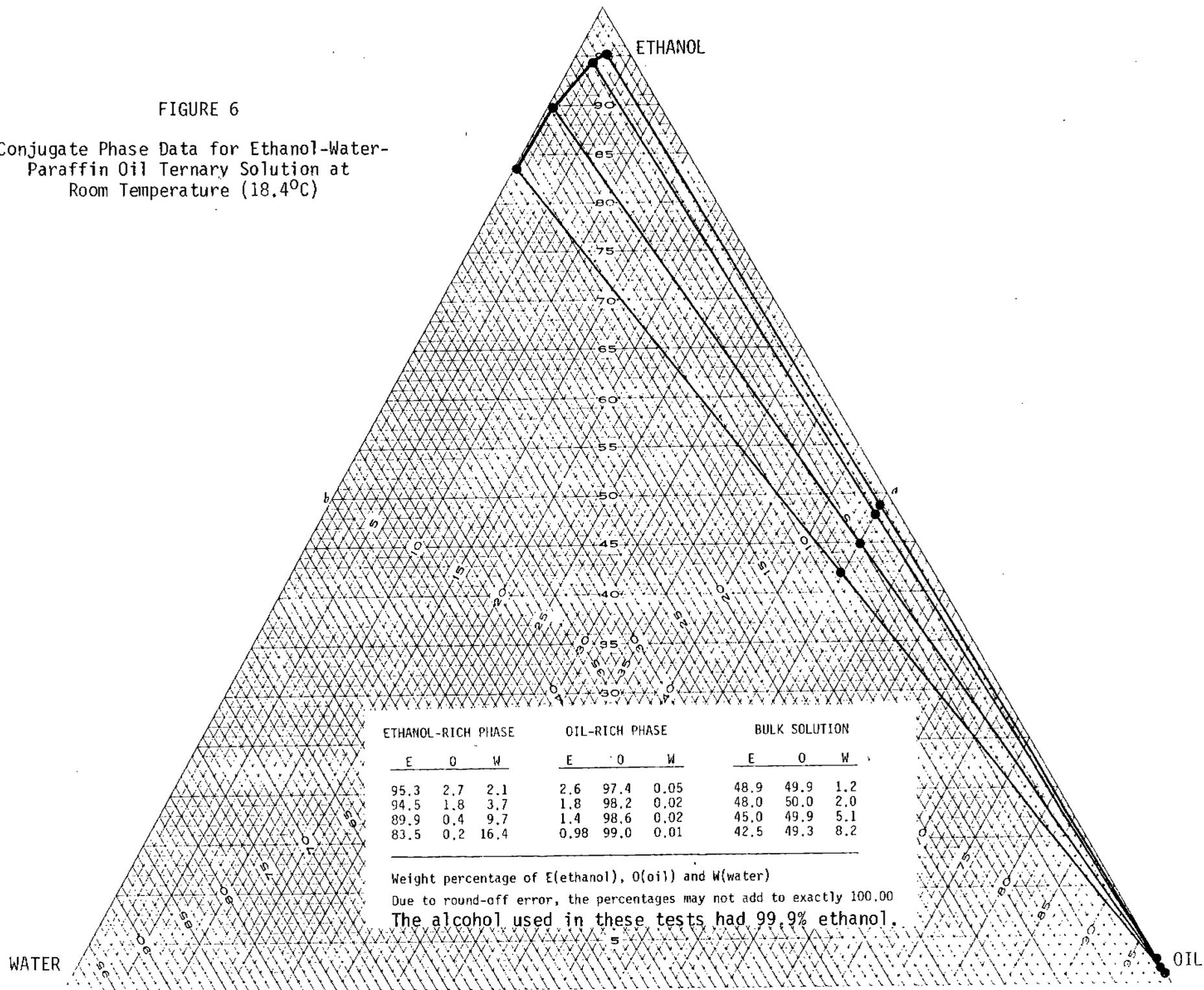
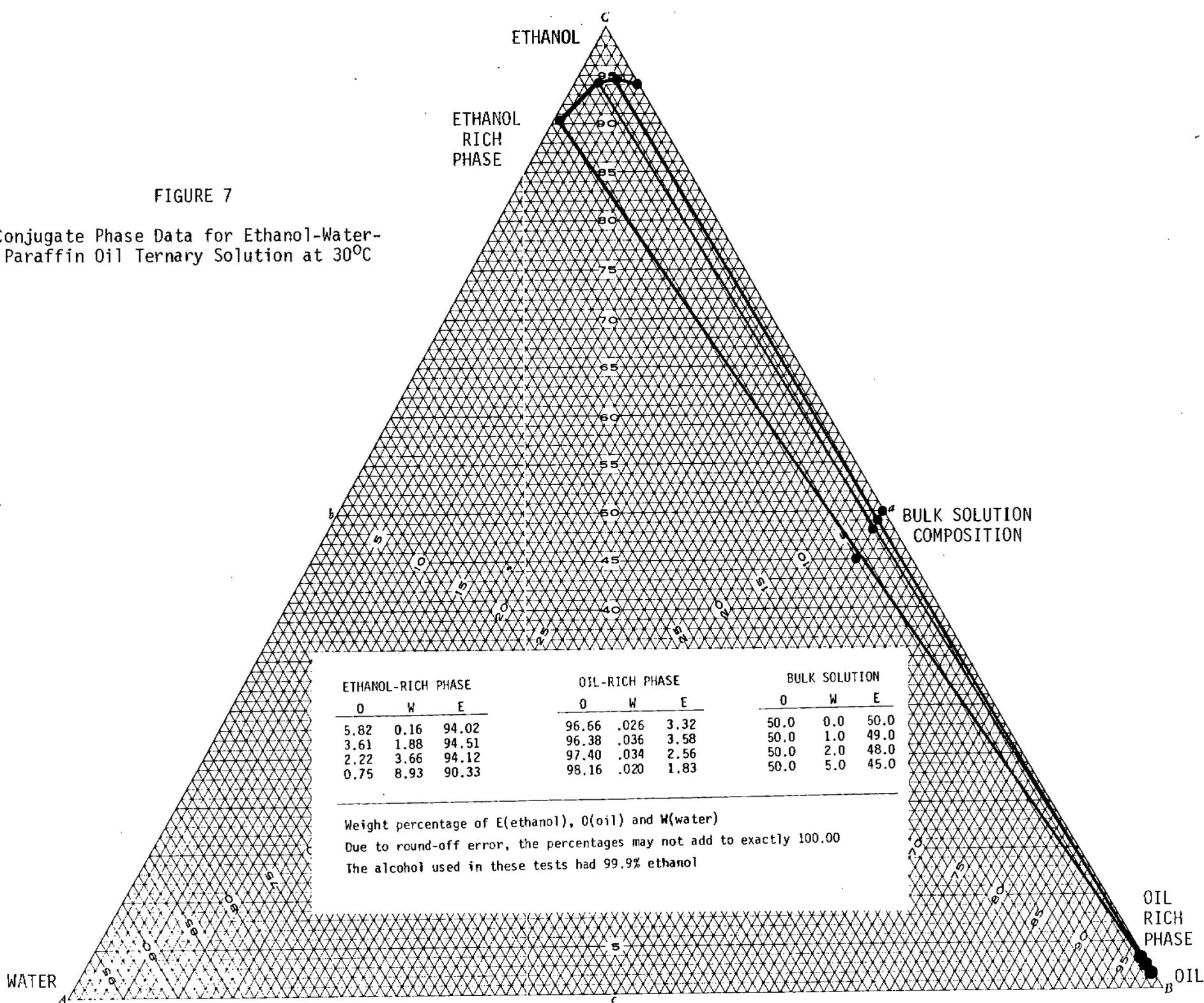
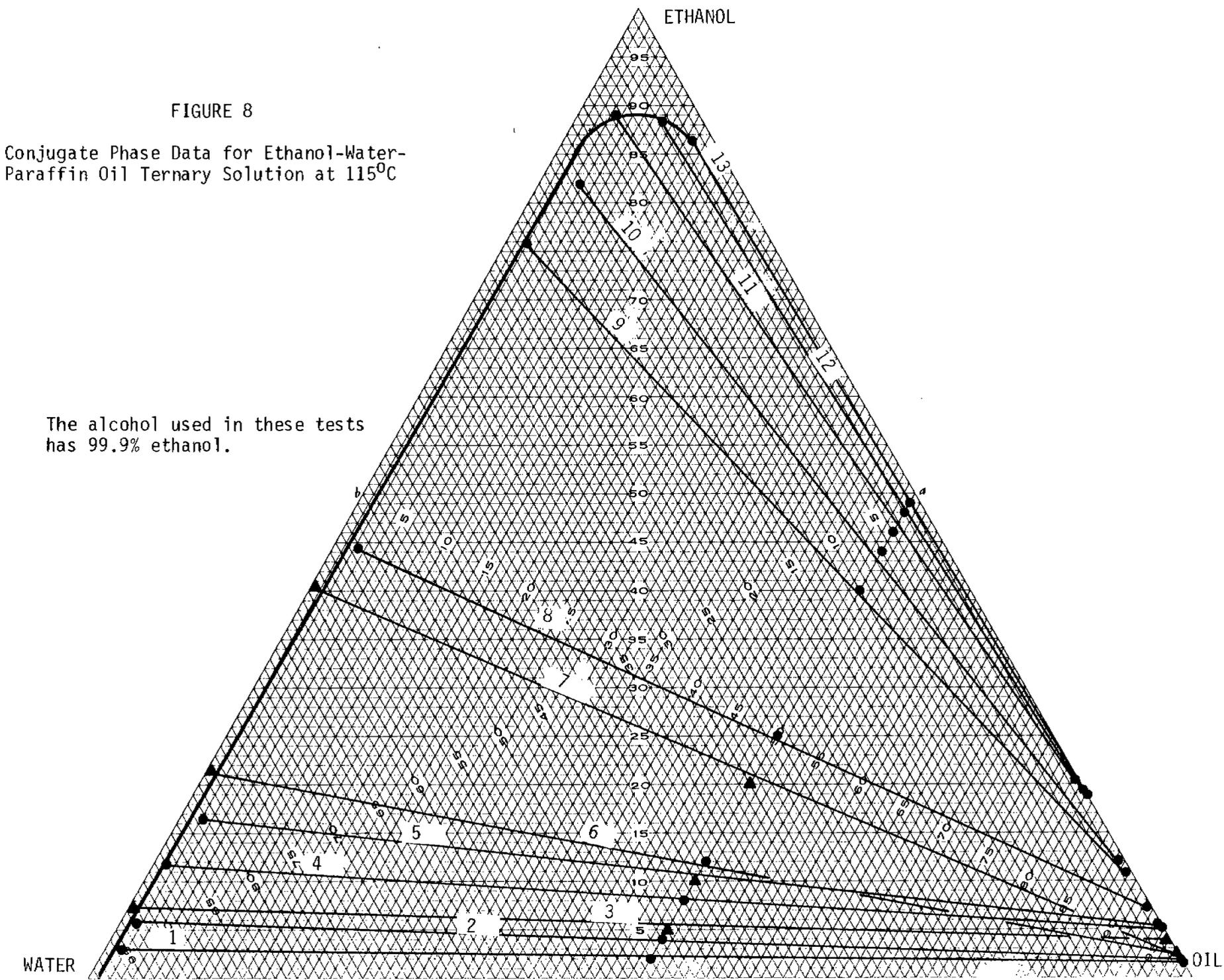


FIGURE 7
 Conjugate Phase Data for Ethanol-Water-
 Paraffin Oil Ternary Solution at 30°C





APPENDICES

A. EXPERIMENTAL PROCEDURES

B. DETAILS FOR THE DESIGN AND ANALYSIS OF THE BASELINE SYSTEM

A. EXPERIMENTAL PROCEDURES

1. The Experimental Setup

The experimental setup used to measure the upper critical solution temperature (UCST) and to determine the composition of conjugate phases is shown in Figure A-1. For temperature up to 90°C a water bath was used while for higher temperatures, a cooking oil bath was used. All the test tubes containing binary or ternary mixtures were closed from the top by means of two different size septums. To ensure that there is no vapor loss and that the septums do not come-off (due to high vapor pressures of ethanol and water at temperatures above 30°C) the septums were held tight by means of ring clamps as shown in the figure. Generally the septums bulged appreciably due to buildup of high vapor pressure in the test tubes at temperatures near 100°C or higher. On some occasions a few septums bursted confirming that there was no loss of material due to leakage. On rare occasions there was some loss of material due to leakage from a few test tubes. This was generally evident by a drop of liquid level in the test tubes. This was attributed to the clamps not being sufficiently tight. These samples were rejected and not analyzed.

To measure UCST, the bath temperature was gradually increased and the temperature at which the solution became a single phase (one clear solution) was noted as UCST. Then the bath temperature was allowed to drop and the temperature at which the solution became cloudy manifesting the start of the two phases was also noted. Typically each UCST measurement was repeated several times and to eliminate any procedural error, each mixture composition was repeated three times or more. The solutions were prepared in sufficient quantity using a digital balance to obtain three significant figures in weighing.

For determination of the tie-line data, bulk ternary solutions of known compositions were prepared in different test tubes. Then these test tubes were sealed from the top by means of septums only, for the conjugate phase data at 30°C or below, and by means of two septums and a clamp for data at 80°C or higher. Typically the same bulk composition was prepared in three separate test tubes. Then the test tubes were placed in a constant

temperature water bath and gently mixed once every 15 minutes for a total of about 8 hours. Then the test tubes were left undisturbed overnight in the bath for about 16 hours. During this period the bulk solution separated into two distinct conjugate phases. Then by means of a syringe with a long needle, samples were gently withdrawn first from the top phase and then after about one-half hour later from the bottom phase while the test tubes were still in the bath. These samples were properly marked and then analyzed using the procedure described below to determine the percentage of oil, water and ethanol in each sample. Typically each sample had to be at least about 2.0 to 2.5 gm for satisfactory analysis.

2. The Analytical Procedure

2.1 Gas Chromotography

During the earlier phase of this project several gas chromatograph columns were investigated to analyze the ternary mixtures of interest. Typically these mixtures comprised of ethanol, water and hexadecane or paraffin/vegetable oil. The different columns that were investigated included:

1. 20% SP-2100, 0.1% Carbowax 1500 on 80/100 Supelcoport, 10' x 1/8" stainless steel, 175^oC maximum temperature.
2. Porapac Q on 80/100 Porapac P, 12' x 1/4" glass, 250^oC maximum temperature.
3. SE-30 on Chromosorb P, 5' x 1/8" stainless steel, 350^oC maximum temperature.
4. 10% Carbowax 20M on 80/100 Supelcoport, 6' x 2 mm stainless steel, 225^oC maximum temperature.

None of these columns was found to be satisfactory because typically the oils and higher paraffins either took too long to come out or never came out thereby loading the column. This was not very surprising particularly because the size, molecular weight and the boiling points of ethanol, hexadecane and oils are significantly different. Secondly, since the oils are typically composed of a number of individual compounds (triglycerides with various

fatty acid groups) it was not possible to use this technique to determine accurately the percentage of oil in a given sample. It was found that the best procedure for analyzing vegetable oils with a GC is apparently to convert the oil to a mixture of its fatty acid methyl esters. Columns are available for separating and analyzing mixtures of fatty acid methyl esters. However, this procedure would result in a chromatogram with a number of peaks representing the vegetable oil, and these peaks would have to be totaled and otherwise interpreted to determine the original amount of vegetable oil, thus greatly complicating the procedure.

To find a better procedure for analyzing mixtures of ethanol-water-vegetable oil, the literature was reviewed and an alternative procedure was found and is discussed below.

2.2 The Titrimetric Procedure

An alternative procedure for analyzing ethanol-water mixtures containing cottonseed oil was found in the literature (2). This technique is quite general and can be useful in analyzing ethanol-water-hexadecane mixtures as well. In this procedure, the sample to be analyzed is split into two parts of known weights. One of these parts is heated in a water bath at about 85°C to boil-off most of the ethanol in the sample followed by placing this part in an oven at about 105°C till the sample reaches a steady weight. By this procedure all the ethanol and water in the sample is evaporated thereby yielding the fraction of oil left in a known sample. Typically, it took about 4 to 6 hours each in reaching the steady weight both in the water bath and in the oven. The other part of the sample is analyzed in the Karl Fischer Titrimeter to determine the percentage of water in the given sample. The percentage of ethanol is then determined by subtracting the percentage of oil and water from 100.

The Karl Fischer Titration is a standard analytical procedure for determining the water content in liquid petroleum products including lubricating oils, gasolines, diesel, jet fuels and absolute alcohol from a distillery. This method is based on a standard ASTM test*. The analytical procedure involves a titration with a standard Karl Fischer reagent in an appropriate solvent system to an electrometric end point. This technique is believed to be very accurate for water concentrations in the 10 to 10,000 ppm range. Karl Fischer titrimeter was also used in determining the moisture content in the ethanol used in our experimental work.

* See for example: "Determining Moisture in Liquid Petroleum Products," Fischer Chemical Company Bulletin No. AB-30, First Issue (0-0822-05/1174).

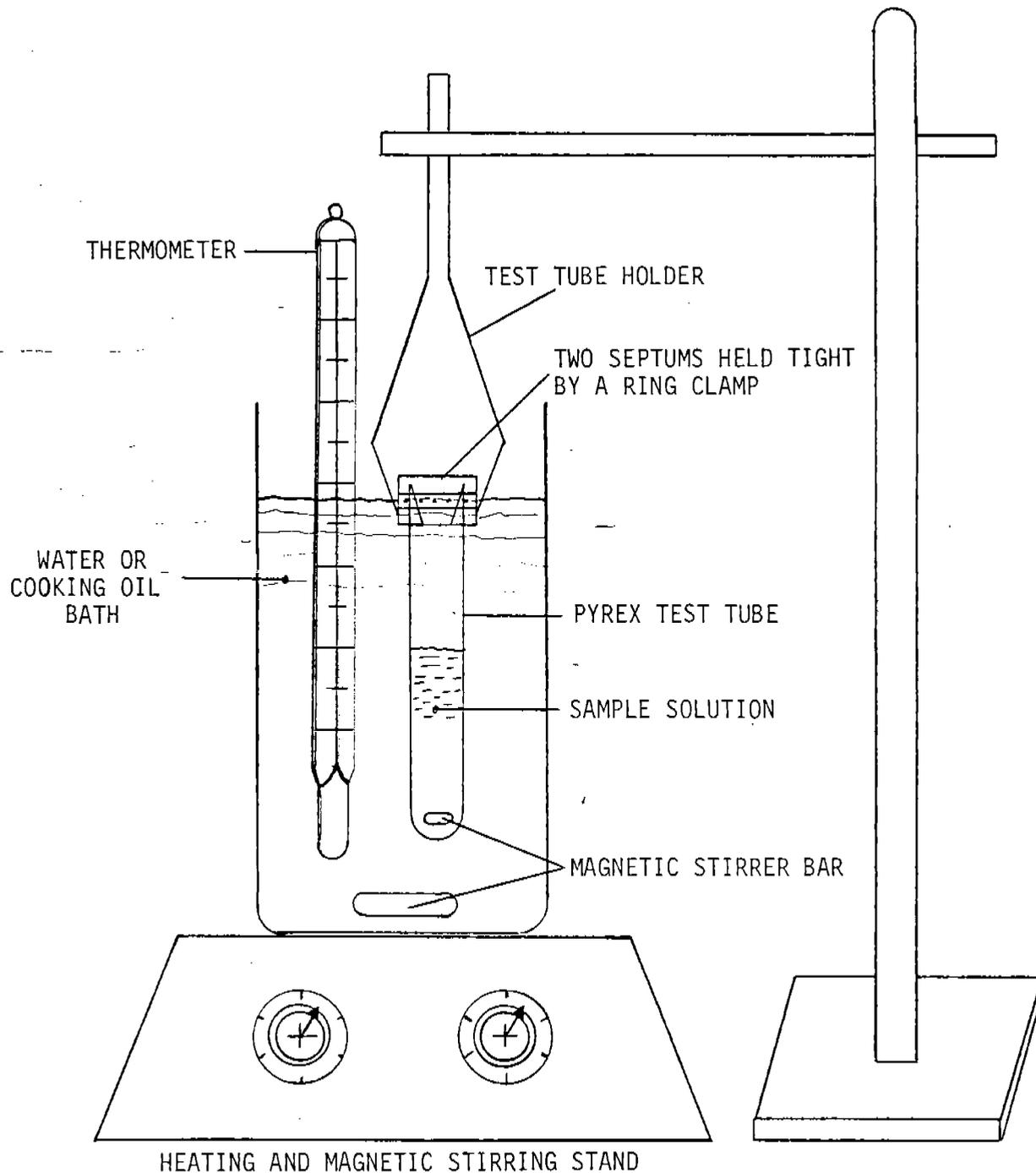


Figure A-1. Experimental Setup for the Determination of Critical Solution Temperature

B. DETAILS FOR THE DESIGN AND ANALYSIS OF THE BASE LINE SYSTEM

This Appendix contains the supporting data for the design and analysis of the base line system presented in Section 4.0 of the main report. In particular, it contains:

1. Material and Energy Balance Equations
2. Mean Physical Properties of ethanol, water and paraffin oil over the desired temperature range (Table B-1)
3. Advantages and disadvantages of different extraction equipment (Table B-2)
4. Correlation of ethanol-water-paraffin oil ternary phase data at 115°C (Figures B-1 to B-3) and at 30°C (Figures B-4 and B-5).

NOMENCLATURE FOR MATERIAL AND ENERGY BALANCE EQUATIONS

Symbols:

m	flow rate in gm/min of numbered stream
x	weight fraction of ethanol
y	weight fraction of extractant
Q	amount of heat transferred in cal/min
c	specific heat in cal/gm- ⁰ C of numbered stream

Subscripts:

1, etc.	stream number or equipment number
H	heater
C	cooler
HX	heat exchanger

MATERIAL BALANCE EQUATIONS

Extractor:

$$\begin{array}{l} \text{total} \\ \text{weight} \end{array} \quad m_6 + m_1 + m_8 = m_2 + m_7$$

$$\text{ethanol} \quad m_6x_6 + m_1x_1 + m_8x_8 = m_2x_2 + m_7x_7$$

$$\text{extractant} \quad m_1y_1 + m_8y_8 = m_2y_2 + m_7y_7$$

Phase Separator:

$$\begin{array}{l} \text{total} \\ \text{weight} \end{array} \quad m_3 = m_4 + m_5$$

$$\text{ethanol} \quad m_3x_3 = m_4x_4 + m_5x_5$$

$$\text{extractant} \quad m_3y_3 = m_4y_4 + m_5y_5$$

Other Parts of the System:

$$m_5 = m_8 + m_9$$

$$m_2 = m_3 = m_{13} + m_{14}$$

$$m_1 = m_4 + m_{10}$$

$$m_1x_1 = m_4x_4$$

$$m_1y_1 = m_4y_4 + m_{10}$$

The phase diagrams at high and low temperatures comprise other relationships needed in the solution of these material balance equations for a specific case.

HEAT BALANCE EQUATIONS

$$Q_{H1} = m_6 c_6 (T_6 - T_0)$$

$$Q_{H2} = m_8 c_8 (T_8 - T_A)$$

$$Q_{H3} = m_1 c_1 (T_1 - T_C)$$

$$Q_{C1} = m_3 c_3 (T_3 - T_B)$$

$$Q_{HX1}^* = m_{13} c_2 (T_B - T_2) = m_8 c_8 (T_A - T_5)$$

$$Q_{HX2} = m_{14} c_2 (T_B - T_2) = m_1 c_1 (T_C - T_4)$$

$$\text{Total heat input} = Q_{H1} + Q_{H2} + Q_{H3}$$

Other necessary relationships for heat exchanger design will be derived by assuming a heat-exchanger effectiveness of 80%.

* Note: Heat exchanger 1 may not be included in the design because the reflux rate is so much smaller than the extract product rate.

Table B-1. Physical Properties of Different Liquids of Interest

The values presented here are the mean values over the desired temperature range.

	Paraffin Oil	Ethanol	Water
Average value of density, gm/ml	0.84*	0.77 (1)	1.0
Average value of viscosity, centipoise	7.0 (2)	0.67 (3)	0.45 (3)
Average value of specific heat, cal/gm-C	0.54 (2)	0.58 (4)	1.00

* Based upon laboratory measurements at 20°C and 85°C.

- (1) American Institute of Physics Handbook, McGraw-Hill Company, New York, 1957.
- (2) J.B. Maxwell, Data Book on Hydrocarbons, D. Van Nostrand Co., Inc., New York, 1958.
- (3) O.W. Eshbach, Handbook of Engineering Fundamentals, John Wiley and Sons, New York, 1975.
- (4) Marks Handbook of Mechanical Engineers, 7th Edition, 1967, pp. 4-11.

Table B-2. Advantages and Disadvantages of Different Extraction Equipment

Class of Equipment	Advantages	Disadvantages
Mixer-settlers	Good contacting Handles wide flow ratio Low headroom High efficiency Many stages available Reliable scaleup	Large holdup High power costs High investment Large floor space Interstage pumping may be required
Continuous counterflow contactors (no mechanical drive)	Low initial cost Low operating cost Simplest construction	Limited throughput with small density difference Cannot handle high flow ratio High headroom Sometimes low efficiency Difficult scaleup
Continuous counterflow (mechanical agitation)	Good dispersion Reasonable cost Many stages possible Relatively easy scaleup	Limited throughput with small density difference Cannot handle emulsifying systems Cannot handle high flow ratio
Centrifugal extractors	Handles low density difference between phases Low holdup volume Short holdup time Low space requirements Small inventory of solvent	High initial costs High operating costs High maintenance cost Limited number of stages in single unit

SOURCE: R.B. Ake11, Chem. Eng. Progr., 62 (9):50 (1966).

Figure B-1. Correlation of Ethanol-Water-Paraffin Oil Ternary Phase Data at 115°C

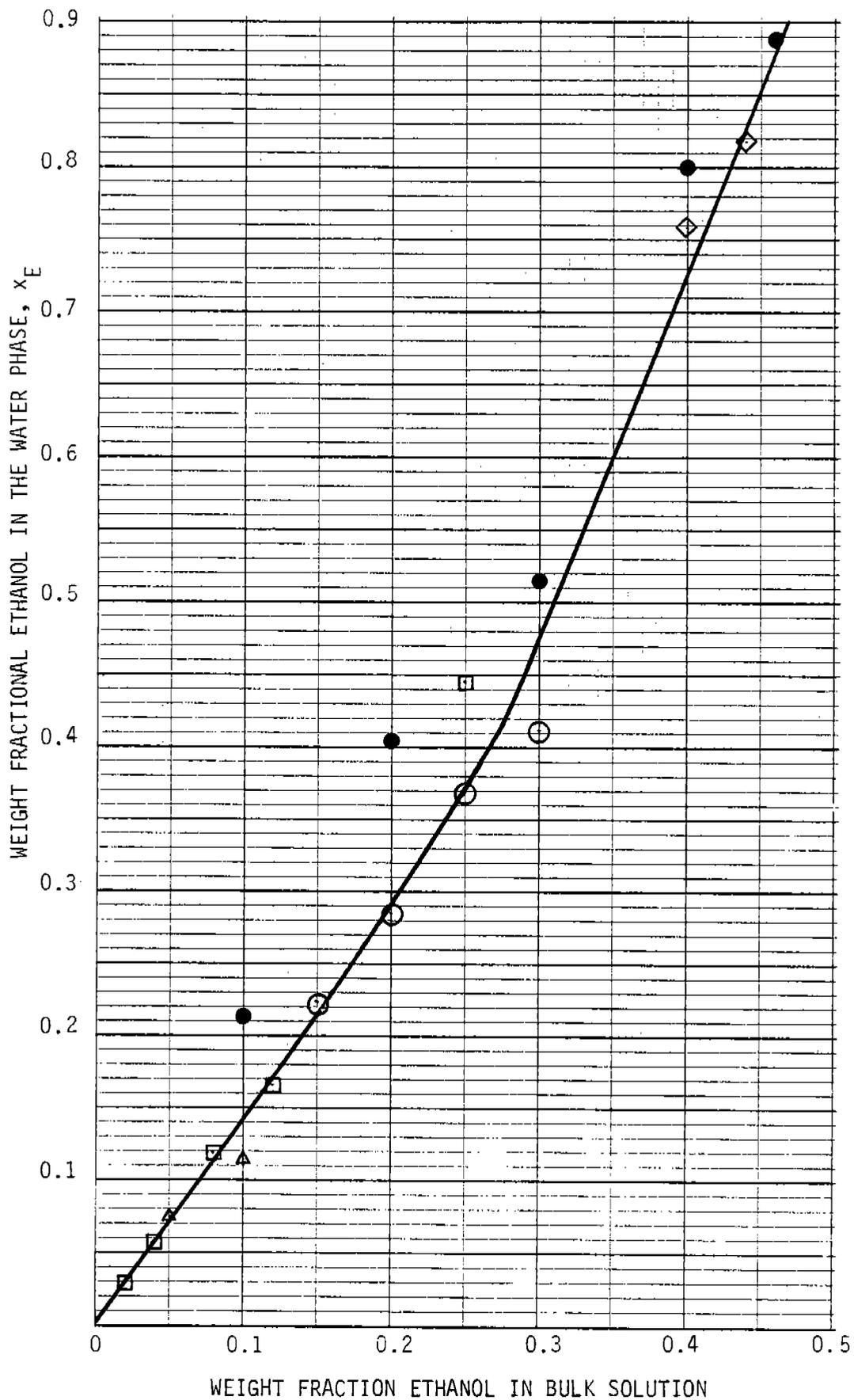


Figure B-2. Correlation of Ethanol-Water-Paraffin Oil Ternary Phase Data at 115°C

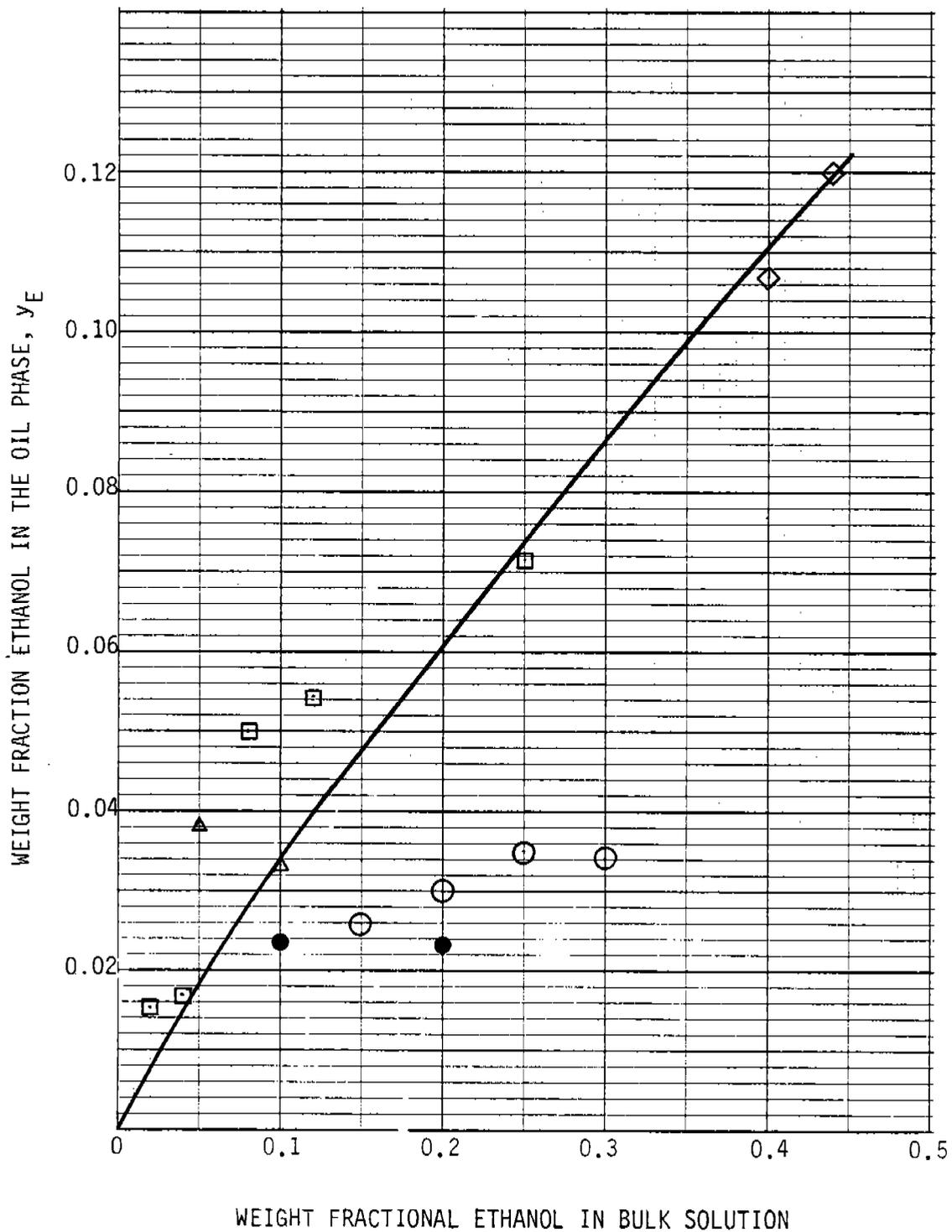


Figure B-3. Correlation of Ethanol-Water-Paraffin Oil Ternary Phase Data at 115°C

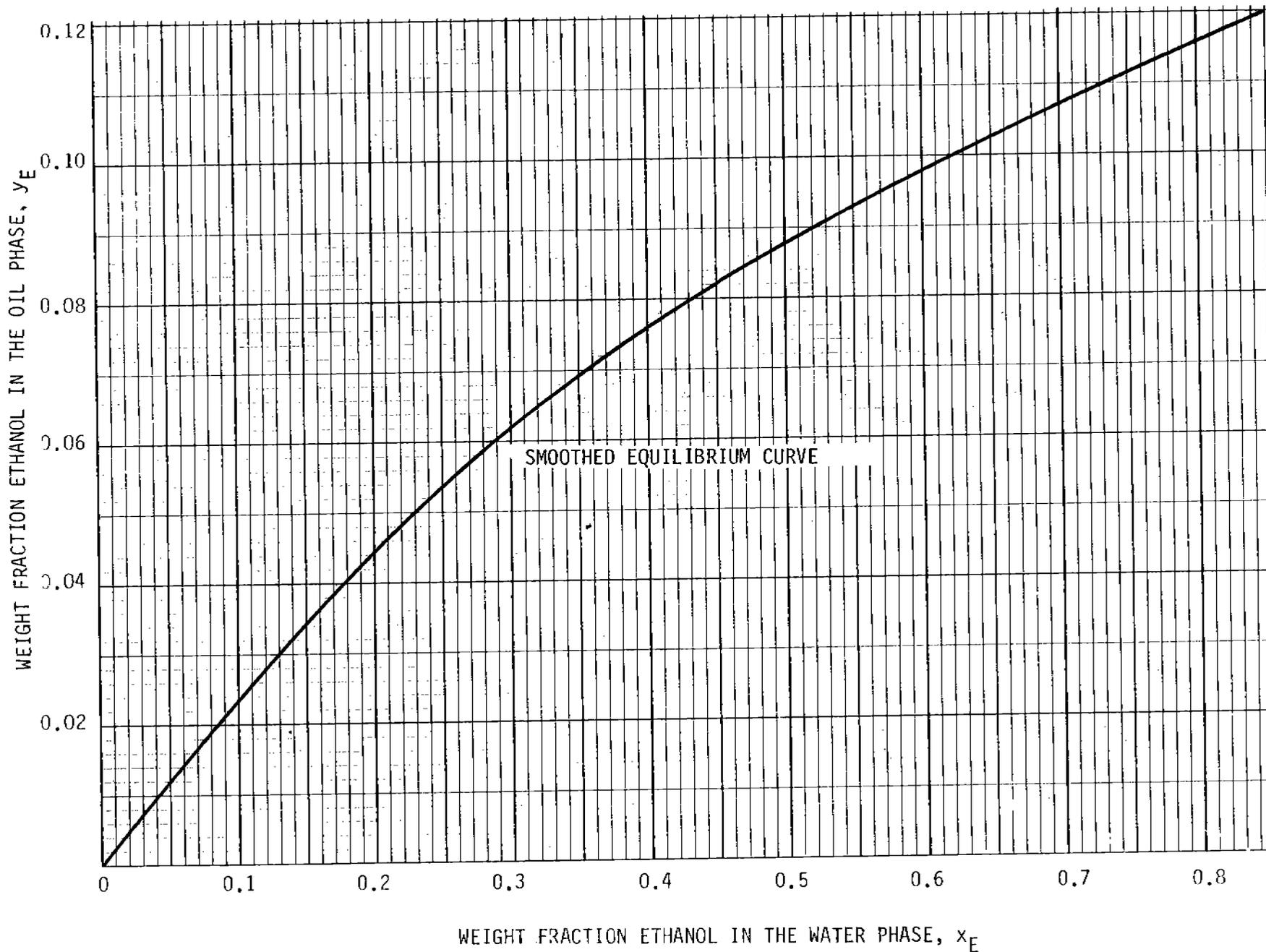


Figure B-4. Correlation of Ethanol-Water-Paraffin Oil Ternary Phase Data at 30°C

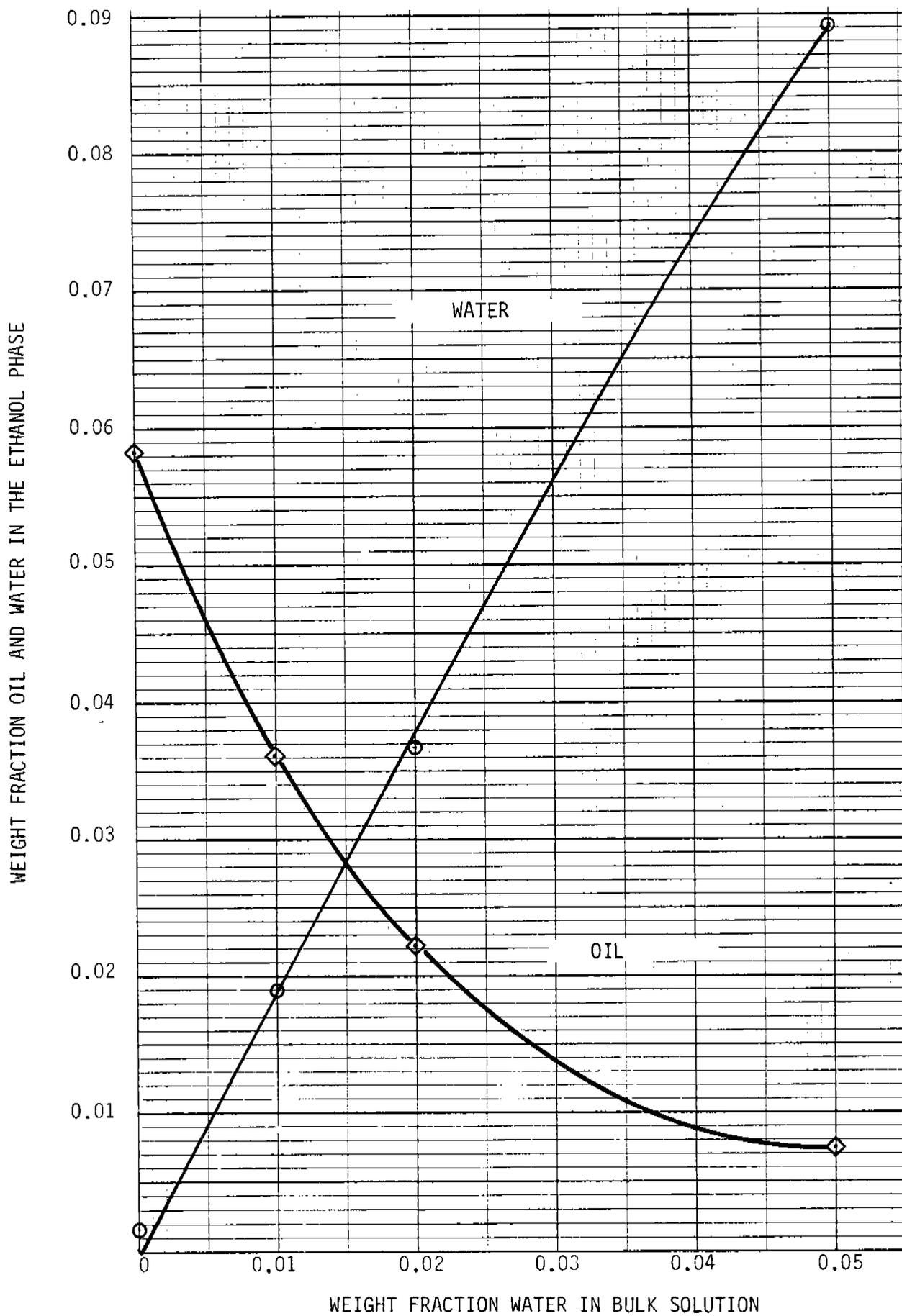


Figure B-5. Correlation of Ethanol-Water-Paraffin Oil Ternary Phase Data at 30°C

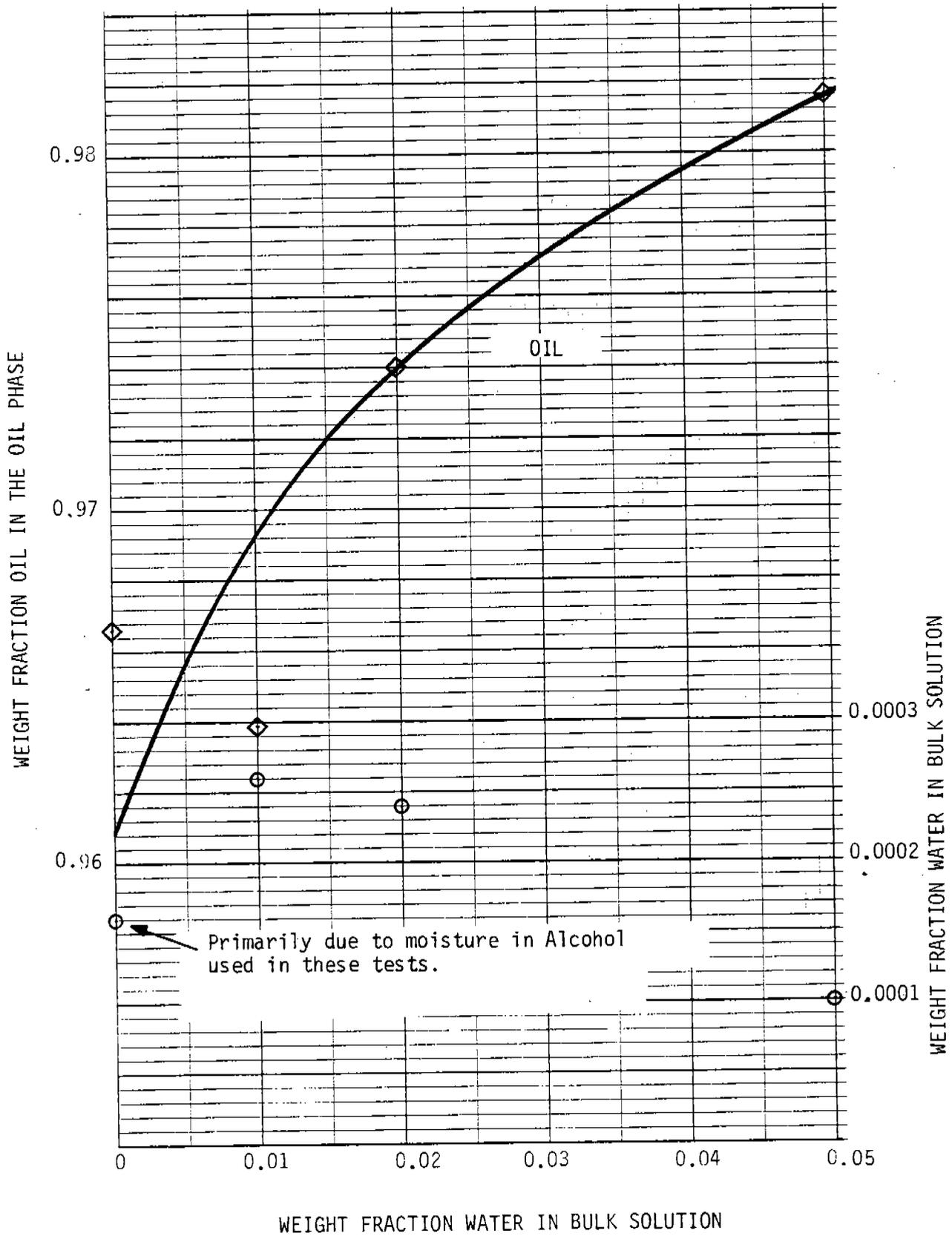
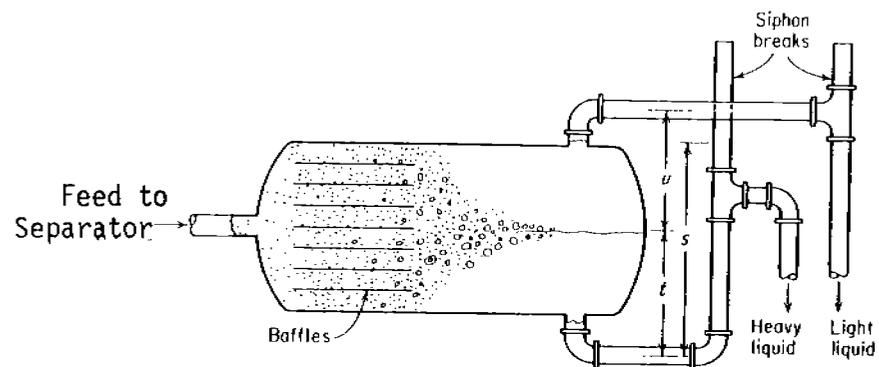


Figure B-6. Schematic Diagram of a Gravity Separator to Recover Two Conjugate Phase Solutions at 30°C



For the proposed application, the light liquid will be the final product while the heavy liquid will be the product extractant for recycling.

Source: Reference 5.