

CO-SOLVENT SELECTION AND RECOVERY

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July 2001

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Abstract

The selection and recovery of two or more solvents (i.e., co-solvents) are studied because of their importance in environmentally responsible processing. A particularly challenging problem arises when the contaminants (or solutes) are comprised of a mixture of volatile and nonvolatile compounds. The nonvolatile components present difficulties in solvent selection while the volatile components give rise to solvent recovery challenges. Traditional approaches such as the Kauri-Butanol test and predictions based on solubility parameters from regular solution theory can result in poor solvent selection when some of the contaminants are nonvolatile. A simple, graphical and rigorous procedure based on Gibbs energies of mixing for all binary mixtures of solvents and contaminants is proposed for choosing solvent/contaminant pairs. This selection procedure is based on the choice of solvent resulting in the lowest solvent/contaminant Gibbs free energy of mixing for a given contaminant.

Nonvolatile contaminants are often easily separated in a single-stage flash vessel. Volatile contaminants, on the other hand, can form homogeneous or heterogeneous azeotropes with commonly used solvents, give rise to distillation boundaries and result in a challenging co-solvent recovery problem. A systematic procedure for the synthesis, design and economic analysis for co-solvent recovery is presented. Residue curve maps are used to identify distillation boundaries and to generate a conceptual process flowsheet for co-solvent recovery. Equipment sizes for the separators and auxiliaries (i.e., condensers, reboilers, decanters, etc.) are determined and capital investment, installation and operating costs are calculated.

The removal of oil-water emulsions from the surface of machined metal parts using n-propyl bromide (NPB) and isopropyl alcohol in a closed-loop degreaser is used to illustrate the proposed methodology of co-solvent selection and recovery. Analysis shows that the Kauri-Butanol test and the use of solubility parameters can result in poor solvent selection. In contrast, the proposed methodology shows that NPB is competitive with banned solvents like chlorodifluoro, fluorodichloroethane (CFC-113) and trichloroethane (TCA) and highly regulated solvents such as perchloroethylene (PCE), trichloroethylene (TCE) and is a good solvent for the removal of machining oils while IPA is a good solvent for removing water. Separation of mixtures of NPB/IPA/water is difficult because of the presence of three binary and one ternary azeotrope that create three distinct distillation regions as well as regions of vapor-liquid-liquid behavior. It is shown that these distillation boundaries preclude direct water separation and that a two-distillation sequence with decantation is required to cross boundaries and recover both solvents. A variety of geometric illustrations are presented to elucidate key concepts.

1. Introduction. The use of organic solvents in cleaning operations is still misunderstood because of associated potential environmental and health hazards (see, Koelsch, 1998; Sauer and Tazi, 1998). Traditionally, solvent cleaning was performed in systems open to the atmosphere, resulting in large volatile organic component (VOC) emissions. These emissions resulted in solvents like chlorodifluoro, fluorodichloroethane (CFC-113), trichloroethane (TCA), perchloroethylene (PCE), trichloroethylene (TCE) and their derivatives being designated ozone-depleting compounds and their use either being banned or highly regulated by legislation (e.g., Montreal Protocol, 1987; Clean Air Act, 1990; Clean Water Act, 1996; and other regulations). In response to growing worldwide legislation and environmental consciousness the cleaning industry has looked for alternatives to open-top, organic cleaning through aqueous-based and closed organic-based systems. Unfortunately, many manufacturers have found aqueous cleaning an inadequate replacement for organic-based systems (Otto, 1999; Bruce, 1998). Cleaning performance has been inferior and higher waste and water treatment costs have resulted. Throughout the 1990's, manufacturers such as Serec Corporation have developed more environmentally acceptable closed organic solvent cleaning units that operate with regulated solvents with minimal annual usage and emissions (Gray, 1993). However, even with advances in environmental safety, solvent selection is not approached in a systematic way. Often times the selection of a particular solvent is based on whether or not that solvent is regulated, what solvent competitors are using or what solvent operators and production personnel are comfortable with!

In today's competitive marketplace, manufacturers often need to remove multiple contaminants between and after manufacturing stages (Otto, 1999; Burt, 1999). Because current cleaning capabilities, even in modern closed-loop systems, are generally limited to the removal of one type of contaminant at a time, the presence of two or more classes of contaminants frequently results in high production costs (Rasmussen, 2000). By mixing two solvents to form a "co-solvent mixture," a single cleaning step can be constructed to remove multiple impurities. This single cleaning step has the potential to reduce costs for the manufacturer because of time and energy savings and can reduce solvent use, emissions and waste streams as well. However, co-solvent cleaning usually creates solvent recovery challenges because some contaminants in these systems are volatile.

The objectives of this research are 1) to develop a mathematical framework for co-solvent selection, 2) to synthesize and design the processing equipment necessary for the separation and recovery of co-solvent mixtures from contaminants, and 3) to evaluate the economics of co-solvent cleaning and recovery. The cleaning example used in this study consists of removing oil-water emulsions from machined metal parts using a co-solvent mixture of a halogenated organic solvent and an alcohol. While these emulsions represent typical multi-contaminant systems in metal working, clearly, other classes of cleaning problems can be addressed using the methodology developed in this work.

2. Cleaning Processes. In this section, we briefly summarize the operation of several common organic-based cleaning systems that have found use in a variety of industries such as the newspaper industry, electronics, plastic component and metal part manufacturing, medical equipment industries, airplane manufacturing and other industries.

Open-Top Cleaning Systems. Open-top vapor degreasers consist of a heated bath in a tank open to the atmosphere that creates a zone of vapor solvent for cleaning. Cooling coils at the top

of the tank are used to condense vapor and prevent it from escaping to the workplace. Any contaminants removed during cleaning are accumulated in the bath and the open-top vapor degreaser can continue to operate until a specific contamination threshold is met. This type of cleaning system does not have solvent-contaminant separation capabilities and can result in large VOC emissions.

Airtight Cleaning Systems. An airtight cleaning system is simply an open-top vapor degreaser with an enclosed hood over the heated bath to further prevent VOC emissions to the environment. Once the bath in these systems is contaminated, the solvent is removed, disposed of as waste and fresh solvent is added, resulting in a continuous solvent usage and cost. Solvent replacement for high production facilities may occur as often as twice a month, making change out a costly method for solvent management in these systems.

Closed-Loop Cleaning Systems. In closed-loop degreasing systems solvent is maintained in a closed heated vessel called a vapor supply tank, which is used to vaporize solvent for degreasing in an adjacent cleaning chamber. Contaminants removed during cleaning are also collected in this vapor supply tank so the solvent becomes 'dirty' over time. Again, cleaning can continue until the solution meets or exceeds some prescribed contamination threshold. However, the difference between closed-loop and other systems is the fact that, when isolated, the enclosed vapor supply tank can also serve as a batch flash vessel for separating solvent from nonvolatile contaminants.

3. Solvents. A 'good' solvent must readily dissolve contaminants, rinse well, dry quickly, be economical and comply with health, safety and environmental regulations. Cleaning equipment manufacturers have always been interested in finding a small collection of 'good' solvents for a wide variety of applications and for many years TCA and CFC-113 fit the bill. They were heavily used because of their superior performance and are still considered by many to be benchmarks for cleaning solvents. However, studies have shown that these two compounds belong to a class of chemicals that are toxic to humans and result in significant damage to the earth's stratosphere in the form of ozone depletion. As a result, TCA and CFC-113 are now banned substances and have since been replaced by regulated solvents such as perchloroethylene (PCE), trichloroethylene (TCE), HCFC's, volatile methyl siloxanes and terpenes in aerosol form. However, with ever growing legislation, cleaning manufacturers and their customers often find managing regulated solvents like PCE and TCE a difficult task riddled with headaches. Thus, there has been recent interest in the use of non-regulated and/or more environmentally friendly solvents like n-propyl bromide (NPB) and inseparable isomers of methoxy-nonafluorobutane ($C_4F_9OCH_3$) or hydrofluoroethers (HFE). NPB is a non-regulated solvent with cleaning capabilities similar to TCE and PCE. However, it is not clear how long NPB will remain a non-regulated substance. HFE's, on the other hand, are a class of compounds marketed by the 3M Company (1996) more as rinsing agents than as solvents since they are often mixed with trans, 1,2-dichloroethylene and sold in a variety of nonazeotropic and azeotropic co-solvent cleaners. Isopropyl alcohol (IPA) has long been an accepted cleaning reagent in the medical industry and for water removal. It is important to note the distinction between the cleaning industry's perspective of co-solvents (i.e., a binary mixture of cleaning and rinsing agents) and the meaning of co-solvents in this work (i.e., a binary mixture of two cleaning agents). In this work, we study the performance of six common solvents in the cleaning industry – CFC-113, TCE, PCE, NPB, HFE and IPA – for use in co-solvent cleaning.

It is also important to understand that the temperature selected for cleaning can depend on a number of factors – the temperature which parts can tolerate without swelling or other damage, the solvent(s) that are used, their flammability or flash point limits, etc. In particular, the vapor pressures of the components in solution are important for designing closed-loop vapor degreasing systems because emissions are directly related to the vapor pressure of the solvent(s) used. The less volatile a solvent is, the more efficient the vapor recovery cycle of the cleaning chamber is resulting in the lowest achievable operating emissions. Solvents with low volatility can be recovered effectively with inexpensive liquid ring vacuum pumps, while solvents with high volatility require more expensive mechanical vacuum pumps to achieve similar emission rates. The type of vacuum recovery equipment directly determines, for the most part, overall system cost, programming requirements and utility needs.

4. Contaminants in Metal Working. The representative example we have selected to study in this work is the tasks associated with cleaning machined metal parts (e.g., parts cut to a specific geometry, bearings, drawn tubes or coils for heat exchange equipment, etc.) that contain an oil-water emulsion on the surface. The purpose of the emulsion in metal working is to provide maximum cooling with water and at the same time have the oil impart some lubricating properties so that friction between the moving chip and the contact surface of any cutting tool is reduced (Forbes, 1943). From an OSHA perspective, a high percentage of water in the emulsion (i.e., as much as 85 % by volume) prevents the oil from misting into the atmosphere exposing operators to potentially hazardous materials. As a result, the part being machined has a working surface that contains an inorganic contaminant, water, and an organic contaminant, oil. The overall cleaning strategy is to use an alcohol to remove the water and an organic solvent to remove the oil.

Mineral and vegetable oils are both used in machining emulsions. The most commonly used oils are refined paraffinic (C_nH_{n+2}) or naphthenic (C_nH_n) oils (Natchman and Kalpakjian, 1985), which are classified by tests for A.P.I. gravity, viscosity and flash point. Vegetable oils, on the other hand, consist of fatty acids and are used for their profound effect on the surface tension of water. Oleic acid or 9-Octadecenoic acid ($C_{18}H_{34}O_2$) is a good example of a vegetable oil used in machining.

5. Solvent Selection and Related Challenges. The choice of solvents for removing organic and inorganic contaminants in cleaning operations must take into account a variety of interrelated issues – solubility, heat and mass transfer, solvent recovery and reuse, environmental considerations, health and safety regulations, economic operation, etc. Remember a desirable solvent must readily dissolve contaminants, rinse clean and dry quickly. Moreover, solvent recovery should be economical.

5.1. Solvent Selection. While solvent selection in the cleaning industry has largely been driven by legislation in recent years, systematic scientific screening of potential solvents has been primarily based on standardized laboratory tests like the Kauri-Butanol test and predictions based on solubility parameters from Scatchard-Hildebrand theory (Scatchard, 1949; Hildebrand, 1929). Unfortunately, these screening procedures can lead to incorrect solvent choices for one reason or another and result in poor process performance.

5.1.1. The Kauri-Butanol Test. Solvent manufacturers often classify hydrocarbon solvents by standard ASTM experimental procedures such as the Kauri-Butanol test. The standard test for determining the Kauri-Butanol number of a potential solvent is a laboratory procedure outlined in ASTM designation D 1133-94 and is based on the titration of a solution of Kauri resin and n-butyl alcohol with a solvent until a defined degree of turbidity is met. The number of milliliters of solvent required to reach the desired degree of turbidity is the Kauri-Butanol number of the solvent. Toluene, which is used as a standard reference solvent, has a Kauri-Butanol number of 105. Table 1 gives a ranked list of Kauri-Butanol numbers for some common cleaning solvents.

Table 1: Kauri-Butanol Numbers for Common Cleaning Solvents

Solvent	Kauri-Butanol Number
TCE	129
NPB	126
PCE	90
CFC-113	31
HFE-7100	10

While ASTM recommends this Kauri-Butanol procedure for selecting solvents for paint and lacquer formulations, it is not suitable for other contaminants such as oils and greases. Unfortunately, many part manufacturers are unaware of this and, as a result, make poor solvent selection decisions. Notice that the Kauri-Butanol number for CFC-113 is considerably lower than that for TCE, PCE or NPB suggesting that CFC-113 is a weak solvent. However, this prediction is inconsistent with industrial experience with CFC-113 as a superior cleaning solvent for a wide variety of contaminants.

5.1.2. Solubility Parameters. Regular solution (or Scatchard-Hildebrand) theory and its extensions are well-known methods for screening solvents with well-known shortcomings. However, it is generally accepted that chemicals that have solubility parameters that are nearly the same can be considered completely miscible and, based on this, suitable solvents are those that have solubility parameters close to that of a given contaminant. For volatile contaminants, solubility parameters can usually be calculated with relative ease and accuracy. On the other hand, for nonvolatile contaminants such as oils and greases, solubility parameters cannot be easily determined. Extensive work by Barton (1975) suggests that solubility parameters of nonvolatile solutes can be determined by other methods – for example, by measuring intrinsic viscosity. However, of the methods available, none are considered simple, making the application of regular solution theory to oils and greases difficult and potentially inaccurate.

To illustrate potential difficulties, the solubility parameter for paraffinic oil ($C_{15}H_{32}$) was calculated at various cleaning temperatures (i.e., 90% of the solvent boiling point at 500 torr). For each temperature, the solubility parameter of the paraffinic oil was between 7.46 and 7.84 (cal / cm^3)^{1/2}. The solubility parameters for the solvents at their respective cleaning temperatures are given in Table 2.

A direct comparison of the solubility parameters listed in Table 2 shows that the solvent with the closest solubility parameter to 7.46 - 7.84 (cal / cm³)^{1/2} is CFC-113, followed by NPB and then HFE-7100. However, HFE-7100 is known to be a much poorer cleaner of oils than PCE and TCE, which have solubility parameters between 8.95 and 9.14 (cal / cm³)^{1/2}. Moreover, the simple test of mixing equal amounts of paraffinic oil and HFE-7100 by volume in a beaker shows that resulting mixture forms two liquid phases, clearly indicating that HFE-7100 is a poor solvent for cleaning paraffinic oil. Therefore, regular solution theory should be used with caution for solvent selection when any of the contaminants (or solutes) is nonvolatile. Physical property data, group contribution and modeling calculations for this example can be found in Finger (2001).

Table 2: Solubility Parameters for Common Cleaning Solvents

Solvent	Cleaning Temperature, °F	Solubility Parameter, (cal / cm ³) ^{1/2}
PCE	233.10	9.14
TCE	171.90	8.95
NPB	143.82	8.75
CFC113	104.70	7.22
HFE-7100	127.60	6.33

5.1.3. Binary Gibbs Energies of Mixing. A simple, graphical and more rigorous way of screening solvents is to use comparative Gibbs free energies of mixing for binary pairs of solvents and contaminants. The rationale behind solvent selection in this case is based on the choice of solvent resulting in the lowest solvent-contaminant Gibbs free energy of mixing for a given contaminant. An extension of this approach based only on binary Gibbs energies of mixing has been used to develop an automatic initialization procedure for multiphase equilibrium flash calculations (see Lucia, et al. 2000) and is presently used in the Aspen Plus simulator. Concepts relevant to solvent selection will be illustrated shortly.

For any mixture at any composition, the Gibbs free energy of mixing is calculated using the equation

$$\Delta G = G^I + G^E \quad (1)$$

where

$$G^I = RT \sum x_i \ln x_i \quad (2)$$

$$G^E = RT \sum x_i \ln \gamma_i \quad (3)$$

and where ΔG is the Gibbs free energy of mixing, G^I is the ideal Gibbs free energy of mixing, G^E is the excess Gibbs free energy of mixing, x_i and γ_i denote the mole fraction and activity coefficient of the i th component, R is the gas constant and T is the absolute temperature. Dimensionless Gibbs free energy of mixing ($\Delta G/RT$ vs x) curves can be easily constructed for

the purpose of evaluating the cleaning capabilities of various solvents using activity coefficients generated by the NRTL equation (Renon and Prausnitz, 1969). Figure 1 shows the dimensionless Gibbs free energy of mixing for the paraffinic oil ($n\text{-C}_{15}\text{H}_{32}$) and the five organic solvents listed in Table 1.

From Fig. 1, the ranked list of solvents for removing paraffinic oil, from best to worst consistent with Gibbs free energies of mixing, is CFC-113, PCE, TCE, NPB and HFE, which is more in line with industrial experience. Note that this ranked list of solvents is considerably different than those predicted by Kauri-Butanol test and regular solution theory and consistent with industrial experience. Moreover, note that there are only slight differences in the solvent/contaminant Gibbs energies of mixing of the first four solvents over the entire range of composition, clearly showing that the non-regulated solvent NPB is a competitive solvent for removing paraffinic oil.

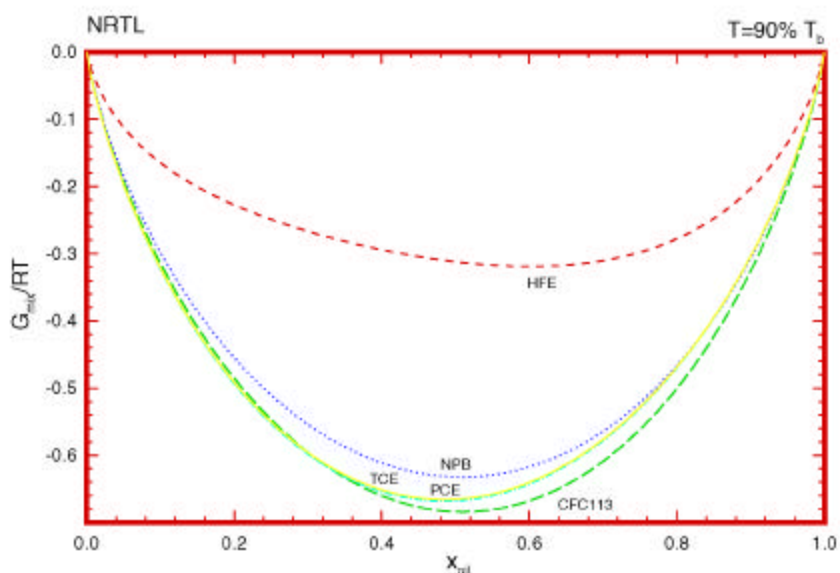


Figure 1: Gibbs Energy of Mixing for Paraffinic Oil/Solvent

Co-Solvent Selection. We begin our study of co-solvent selection with the NPB/IPA/oil/water system. For each of the four components, a total of six binary pairs are possible. Nonideal liquid phase behavior is modeled using the NRTL equation and the corresponding dimensionless Gibbs energies of mixing for all binaries at 170.33 F (350 K) and 500 torr are shown in Figure 2.

A great deal of information can be extracted from Figure 2. First, it is important to note that mixtures of NPB and IPA are miscible over the entire composition range. Second, the paraffinic oil-NPB curve also exhibits complete miscibility over the entire composition range and has the lowest Gibbs free energy of mixing - indicating NPB is a good solvent for oil removal. In contrast, the Gibbs free energy of mixing curve for paraffinic oil-IPA shows liquid-liquid (LL)

behavior and clearly indicates that IPA is a poor solvent for oil removal. Third, IPA and water are completely miscible over the entire composition range while NPB and water are largely

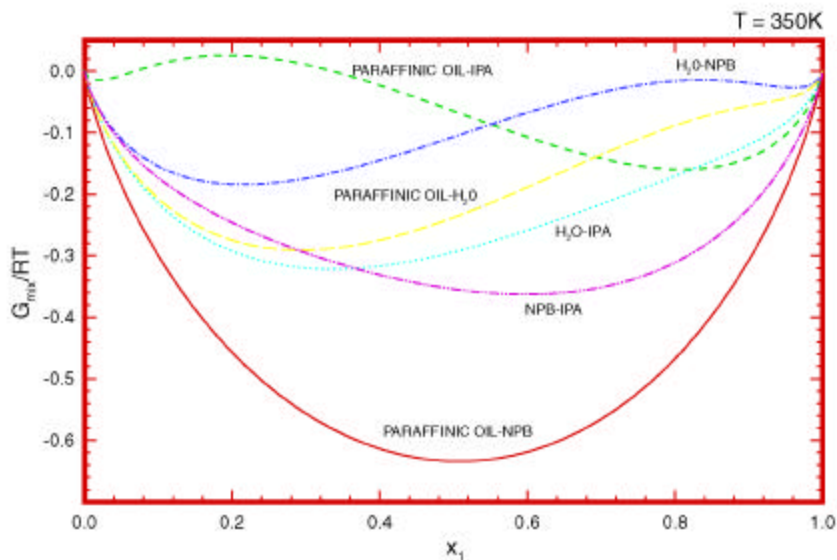


Figure 2: Gibbs Free Energies of Mixing for Paraffinic Oil/H₂O/NPB/IPA

immiscible exhibiting LL behavior over a wide range of composition. This suggests that IPA is the preferred solvent for water removal.

Figures 3 and 4 show the Gibbs free energy of mixing for all solvent/contaminant pairs for the naphthenic oil ($C_{15}H_{30}$)-water and oleic acid ($C_{18}H_{34}O_2$)-water emulsions respectively. The naphthenic oil-water system shows essentially identical behavior to that of the paraffinic oil-water emulsion, with only a slightly higher Gibbs free energy of mixing for the naphthenic oil-NPB pair. This suggests that NPB might be somewhat more effective in removing the lighter weight paraffinic oils. Figure 4, on the other hand, shows that NPB and IPA have similar affinity for oleic acid suggesting that solvent recovery might be more difficult when removing vegetable oils.

6. Co-Solvent Recovery. In many applications it is desirable to maximize the life of any solvent. For oil contaminants in standard single-component solvent cleaning solutions such as perchloroethylene, trichloroethylene and NPB, contamination thresholds as high as 30% by volume can be tolerated before solvent clean up or change out is required (Bruce, 1998). Contamination levels at/or above this threshold will cause contaminants to redeposit on the parts being cleaned. Co-solvent mixtures have been limited to use in open-top and airtight cleaning systems because co-solvent baths operate in exactly the same manner as the pure solvent systems. Solvent is removed as a waste stream and completely replaced when the contamination threshold is met since these cleaning systems are not generally equipped with separation equipment. Even when separation capabilities are available, as in closed-loop systems, solvent

recovery capabilities are limited. This section contains a discussion of the process synthesis, design and simulation of separation equipment needed for co-solvent recovery.

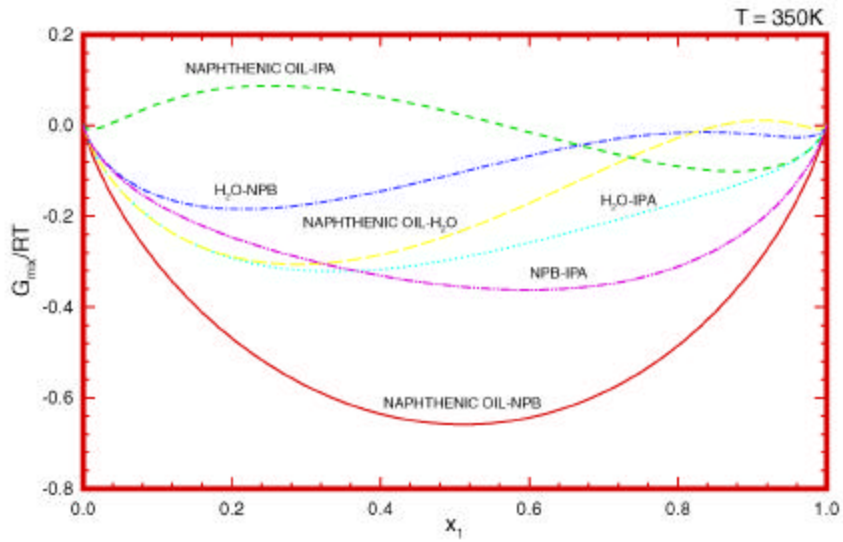


Figure 3: Gibbs Free Energies of Mixing for Naphthenic Oil/H₂O/NPB/IPA

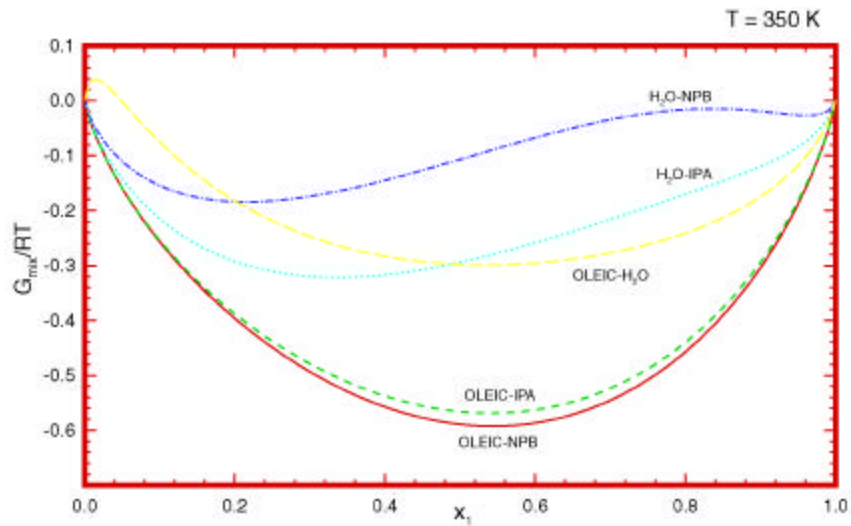


Figure 4: Gibbs Free Energies of Mixing for Oleic Acid/H₂O/NPB/IPA

6.1. Process Flowsheet. The separation of NPB, IPA and emulsion contaminants is presented as a representative example of co-solvent recovery in cleaning operations. Although co-solvent recovery can be used with any of the aforementioned cleaning systems, the proposed separation system that is described is outlined for use with a closed-loop cleaning system. An overall flow diagram for co-solvent recovery is shown in Fig. 5 and consists of the required equipment and product and waste stream flows. In Fig. 5, co-solvent is recycled for continuous cleaning use and the near solvent-free contaminants are removed as waste streams. Each of the major separation tasks in Fig. 5 is discussed in detail in the next few sections.

6.1.1. Batch Flash Tank. Batch flash is a simple, cost-effective method for separating liquids with wide boiling point differences. Oleic acid and the mineral oil contaminants all have relatively high boiling points with essentially no vapor pressure and thus for each of the co-solvent/emulsion mixtures studied, the high boilers (the oils) were completely separated as the bottoms product from a batch flash vessel. The design parameters for the co-solvent batch flash were derived from solvent recovery requirements for a single-solvent closed-loop degreasing systems. A system that processes 900 to 1,500 pounds of clean parts per hour must have separation capabilities of 2 gpm to maintain contaminant-free solvent for continuous production cleaning. Feed is typically made up of a composition of 85mol % co-solvent and 15mol % contaminant. Thus a co-solvent feed contaminated with 6.1 gpm of emulsion can be processed and still meet this design criterion to produce a recovery rate of 2 gpm. Batch simulations for each emulsion system were performed at various temperatures and pressures to determine the most effective separation parameters to meet this 2 gpm recovery goal.

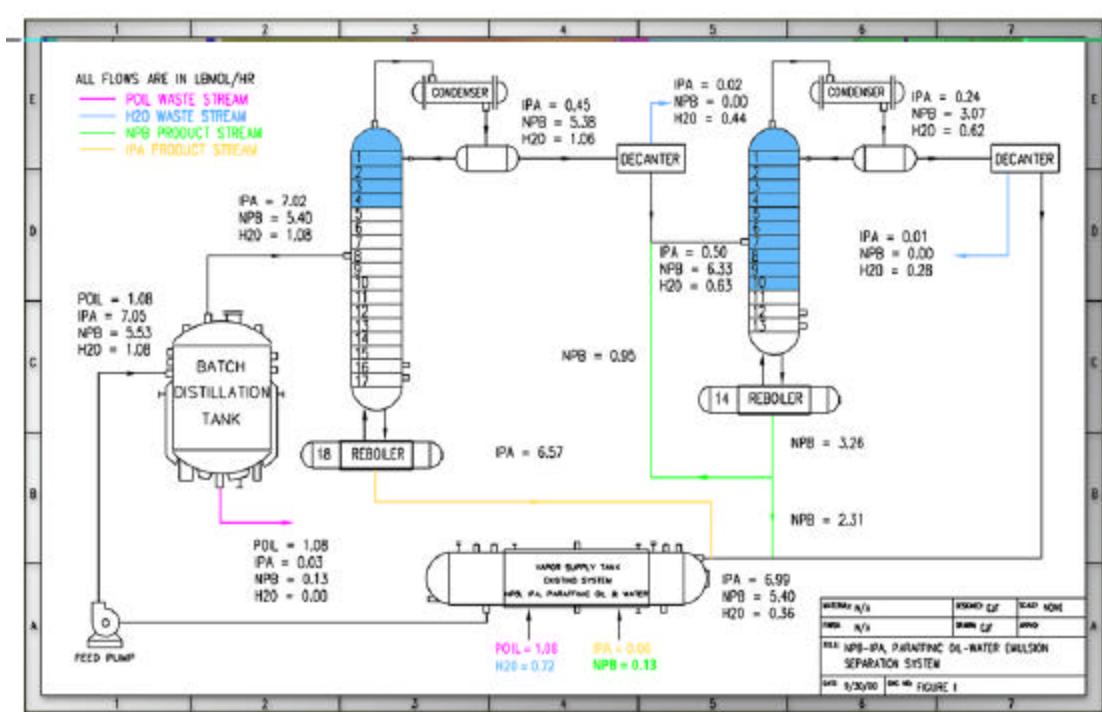


Figure 5: Process Flowsheet for Co-Solvent Recovery System

The batch flash for the co-solvent/emulsion mixture containing the paraffinic oil contaminant completely removes all of the 1.08 lbmol/hr of oil in the feed as bottoms product at a temperature and pressure of 195 °F at 500 torr respectively. A vertical batch flash tank 3.5 ft. diameter by 3.5 ft. straight side can easily perform this separation. The tank is jacketed and fully insulated with 1 in. thick silicone covered insulation and is heated by 50 psi steam. A summary of the material streams for this flash separation is shown in Table 3.

Table 3: Material Streams for Batch Flash Separation of Paraffinic Oil

Stream	Feed	Distillate Product	Bottoms Product
Phase	Liquid	Vapor	Liquid
Molar Flow (lbmol/hr)			
Paraffinic Oil	1.08	0.00	1.08
IPA	7.05	7.02	0.03
NPB	5.53	5.40	0.13
Water	1.08	1.08	0.00

A complete tabulated summary of the separation calculations including heat duty, stream enthalpies, densities, average molecular weights, molar liquid volumes, etc. can be found in Finger (2001). Note that only minimal traces of solvent, 0.03 lbmol/hr (0.4%) of IPA and 0.13 lbmol/hr (2.4%) of NPB, are present in the bottoms waste stream and can be considered consumables.

The co-solvent/emulsion mixtures containing naphthenic oil and oleic acid were also simulated in the same piece of equipment. For the naphthenic oil, the simulation gave identical results to those shown in Table 3. The oleic acid flash separation resulted in higher solvent losses as predicted but required less energy because it was run at a lower temperature of 185°F @ 500 torr. Operating at lower temperatures reduces heat duty requirements and operating costs. Results for the material streams for the oleic acid separation are shown in Table 4 while complete details of the separation can be found in Finger (2001).

Table 4. Material Streams for Batch Flash Separation of Oleic Acid

Stream	Feed	Distillate Product	Bottoms Product
Phase	Liquid	Vapor	Liquid
Molar Flow (lbmol/hr)			
Oleic Acid	1.08	0.01	1.07
IPA	7.05	6.41	0.64
NPB	5.53	5.24	0.30
Water	1.08	0.88	0.21

The bottoms product is a waste stream that removes 99.1 mol % of the oleic acid from the feed along with 19.44 mol % water, 9 mol % IPA and 5.4 mol % NPB.

6.1.2. Co-Solvent Recovery System Synthesis and Design. The distillate product from the batch flash tank is a ternary mixture of IPA, NPB and water and becomes the feed to the NPB-IPA co-solvent recovery system. The behavior of any ternary separation by distillation can be understood using residue curve analysis (Doherty and Perkins, 1978). Figure 6 shows the residue curve map for NPB/IPA/H₂O.

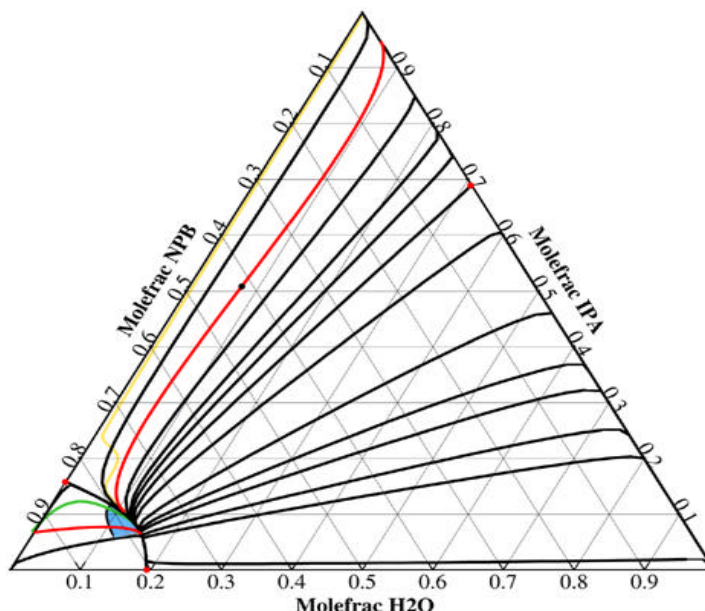


Figure 6: Residue Curve Map for NPB/IPA/H₂O at 500 torr

Figure 6 clearly shows that the feed location (i.e., the black dot), the presence of three binary azeotropes and one heterogeneous ternary azeotrope (i.e., the red dots) and a blue shaded region containing three-phase (VLL) behavior. Table 5 gives the compositions of all azeotropes.

It is well known that the presence of azeotropes can result in distillation boundaries that place limits on the products from a given distillation column. In this system, there are three curved distillation boundaries that connect the ternary azeotrope to each of the binary azeotropes. Thus there are three distillation regions and, as a result, at least two distillation columns are required to produce pure IPA and pure NPB.

Figure 6 also shows the behavior of both an infinite reflux and infinite stage separation system (i.e., the red curves) and a separation system run at finite reflux with a finite number of stages (i.e., the yellow and green curves). Note that there are significant quantitative differences between the two.

Table 5: Azeotropic Compositions for NPB/IPA/H₂O at 500 torr

(NPB, IPA, H ₂ O)	Azeotrope Type
(0.84, 0.16, 0)	Homogeneous
(0.81, 0, 0.19)	Heterogeneous
(0, 0.68, 0.32)	Homogeneous
(0.781, 0.065, 0.154)	Heterogeneous

6.1.3. Direct Water Removal. Complete removal of water from the ternary mixture NPB/IPA/H₂O in a single column is desired but because of the presence of the distillation boundary that runs from the ternary heterogeneous azeotrope to the IPA/H₂O azeotrope and water's affinity for both solvents, this separation is not practical. Note that the feed from the batch flash vessel is located in a distillation region that favors the initial removal of IPA. Moreover, high IPA to water ratios in the feed indicate that the mixture from the vapor supply tank would also have high concentrations of IPA resulting in good inorganic removal in the cleaning unit. Based on these considerations the approach for separating the water directly was considered to be impractical.

6.1.4. IPA Recovery and Decantation. Residue curve analysis for a typical feed mixture clearly shows that pure IPA can be removed as bottoms and that the ternary heterogeneous azeotrope can be taken overhead in a single column. The column required for IPA separation is designated the IPA recovery column (see, Fig. 5) and produces a high purity IPA bottoms stream of 6.57 lbmol/hr (93.6% IPA removal from the feed) and a distillate stream of 6.89 lbmol/hr having the ternary azeotropic composition. An eighteen-stage column with a reflux ratio of 15 is required to produce these product streams and operates as follows. The first stage at the top of the rectification section of the column is a total condenser and the eighteenth stage is the reboiler with the feed located on tray 8. Temperatures range from 160°F in the reboiler to 112°F in the condenser, the pressure is constant at 500 torr, and the column has a diameter of 36 in. with a perforated tray spacing of 18 in. The reboiler is a 4 ft. diameter by 4 ft. straight side vertical tank with a 37.4 ft² auxiliary flash heat exchanger. The reboiler is jacketed and heated with 50 psi steam. This column, the heat exchanger and reboiler are fully insulated with 1 in. silicone covered insulation to contain heat losses. The total condenser area is 312 ft² and is insulated with ¾ in. thick Armaflex insulation material to prevent condensation collection. Product streams for the IPA recovery column are shown in Table 6.

Table 6: Material Balance Streams for IPA Recovery Column

Stream	Feed	Distillate Product	Bottoms Product
Phase	Liquid	Liquid	Liquid
Molar Flow (lbmol/hr)			
Paraffinic Oil	0.00	0.00	0.00
IPA	7.02	0.45	6.57
NPB	5.40	5.38	0.02
Water	1.08	1.06	0.02

The corresponding overall liquid composition profile for the IPA recovery column is shown in Table 7.

Table 7: Overall Liquid Tray Compositions for IPA Recovery Column

Tray Number	IPA	NPB	Water
1	0.0648384	0.78117192	0.1539897
2	0.0686615	0.78064774	0.1506907
3	0.0738303	0.78028883	0.1458809
4	0.0808671	0.78050143	0.1386315
5	0.0903892	0.78202222	0.1275886
6	0.1028946	0.78578143	0.111324
7	0.119686	0.78950557	0.0908084
8*	0.1567804	0.76810974	0.0751099
9	0.1659118	0.77636638	0.0577218
10	0.1742995	0.78506615	0.0406343
11	0.1810312	0.79250795	0.0264608
12	0.1862337	0.79752099	0.0162453
13	0.1934319	0.79687945	0.0096886
14	0.235376	0.75828714	0.0063369
15	0.5274228	0.46554976	0.0070274
16	0.8716804	0.12157825	0.0067414
17	0.974413	0.02089293	0.0046941
18	0.9937396	0.00327004	0.0029903

* feed tray

The IPA bottoms stream is returned to the vapor supply tank for use in the closed-looped degreasing system. Three-phase vapor-liquid-liquid (VLLLE) behavior exists on the top four trays of this column as shown in blue in Fig. 5. The heterogeneous distillate product from the IPA recovery column is sent to a decanter for additional water removal.

The distillate product from the IPA recovery column contains water contamination levels greater than that of IPA resulting in two-phase LLE behavior. Reducing the temperature to cooling water temperatures of 50°F improves the gravity separation. Thus a 4.6 ft² cooling heat exchanger is used to reduce the temperature of the distillate product from 112°F to 50°F for maximum water separation in a decanter. The resulting liquid compositions from the decanter are shown in Table 8. Complete details of the simulation can be found in Finger (2001).

Table 8: Decanter Products for IPA Recovery

Stream	Feed	Outlet Product 1	Outlet Product 2
Phase	Liquid	Liquid 1	Liquid 2
Molar Flow (lbmol/hr)			
IPA	0.45	0.43	0.02
NPB	5.38	5.38	0.00
Water	1.06	0.62	0.44

Liquid 2 from the decanter contains 0.44 lbmol/hr water and is removed from the system as a waste stream. The other liquid phase is processed to recover NPB.

6.1.5. NPB Recovery. Decantation plus the addition of pure NPB allows one to cross a distillation boundary to a region where NPB recovery is feasible. This NPB recovery column produces a high purity bottoms stream of 3.26 lbmol/hr NPB and 3.93 lbmol/hr of a distillate stream with the ternary azeotropic composition. A portion of the NPB bottoms product is recycled and mixed with liquid stream 1 from decanter 1. Fourteen stages and a reflux ratio of 5 are required for this separation with the feed located on the seventh tray. The column operates at temperatures from 115°F in the reboiler to 112°F at the top of the column at a constant pressure of 500 torr, and has a diameter of 18 in. with a perforated tray spacing of 18 in. The reboiler is a 3 ft. diameter by 3 ft. straight side vertical, jacketed tank and heated by 50 psi steam. The column and reboiler are fully insulated with 1 in. thick silicone covered insulation to prevent heat losses. The total condenser has a service area of 67 ft² and is insulated with ¾ in. thick Armaflex insulation. The product streams for the NPB recovery column are shown in Table 9. Complete details of the NPB recovery column simulation are provided in Finger (2001).

Table 9: Material Balance Streams for NPB Recovery Column

Stream	Feed	Distillate Product	Bottoms Product
Phase	Liquid	Liquid	Liquid
Molar Flow (lbmol/hr)			
IPA	0.50	0.24	0.26
NPB	6.33	3.07	3.26
Water	0.63	0.62	0.01

The overall liquid composition profile for the NPB recovery column is shown in Table 10.

Table 10: Overall Liquid Tray Compositions for NPB Recovery Column

Tray	IPA	NPB	H ₂ O
1	0.06107	0.78189	0.15704
2	0.06343	0.78147	0.15511
3	0.06653	0.78103	0.15243
4	0.07067	0.78066	0.14867
5	0.07623	0.78058	0.14319
6	0.08349	0.78193	0.13458
7*	0.09115	0.78988	0.11896
8	0.1031	0.79535	0.10155
9	0.11672	0.80515	0.07813
10	0.12944	0.81769	0.05287
11	0.13805	0.8304	0.03155
12	0.13779	0.84546	0.01675
13	0.11721	0.87519	0.00761
14	0.07154	0.92578	0.00268

* feed tray

The pure NPB bottoms stream of 3.26 lbmol/hr is split and 0.95 lbmol/hr are returned as feed to the NPB recovery column while the remainder is returned to the vapor supply tank of the closed-loop degreasing system. VLLE behavior exists on the top ten trays of the NPB recovery column. The distillate product contains a greater concentration of water than IPA and is cooled to 50°F and sent to a decanter for separation. Again, a 4.6 ft² heat exchanger is sufficient to reduce the temperature of the distillate product from 112°F to 50°F for maximum water separation. The resulting liquid phase compositions are listed in Table 11.

Table 11: Decantation Products for NPB Recovery

Stream	Feed	Outlet Product 1	Outlet Product 2
Phase	Liquid	Liquid 1	Liquid 2
Molar Flow (lbmol/hr)			
IPA	0.24	0.23	0.01
NPB	3.07	3.07	0.00
Water	0.62	0.34	0.28

Liquid 2 from decanter 2 is removed from the system as a waste stream while Liquid 1 is returned to the vapor supply tank along with the recovered IPA and NPB for continuous use in the closed-loop cleaning system.

6.2. Process Economics. Contaminated solvent from cleaning systems without solvent management or separation capabilities must be removed and disposed of as waste. New solvent must be purchased on a continuous basis and there are also high costs associated with hazardous solvent disposal. Initial capital investments for separation equipment can replace these expenses with potential short-term capital payback resulting in long-term savings and responsible environmental practices. This section describes the capital investment, installation and operating costs for using co-solvent cleaning in open-top, airtight and closed-loop degreasers fitted with a co-solvent recovery system.

6.2.1. Capital Investment Costs. A summary of the capital cost analysis for co-solvent recovery for a closed-loop cleaning system capable of processing 900 to 1,500 pounds of clean parts per hour with solvent recovery capabilities of 2 gpm is provided in Table 12.

Capital investment costs have been calculated using equipment costs from local distributors and reference texts (e.g., Peters and Timmerhaus, 1968). All cost adjustments were made for the third quarter of 2000 using the Marshall and Swift (M&S) Equipment Cost Index for the chemical process industry. A more detailed table consisting of price source and M&S index adjustments can be found in Finger (2001). The total capital investment cost shown in Table 12 is approximately the same as that for a new closed-loop degreasing unit in the range of \$ 120,000.00 to \$ 160,000.00 (McCormick, 2001). For existing closed-loop systems this equipment can be added to the cleaning system for the capital cost listed above plus installation expenses.

6.2.2. Installation Costs. For part manufacturers that currently have existing closed-loop degreasing systems, these systems can be upgraded for the use of co-solvents by purchasing the co-solvent recovery system outlined in section 6.1. Since there are many closed-loop systems currently in operation throughout the world, the associated installation costs were determined. A summary of the add-on installation costs for the proposed co-solvent recovery system is provided in Table 13. Installation costs were based on on-site installation. A more detailed table, consisting of required hours and labor prices, can be found in Finger (2001).

6.2.3. Operating Costs. A comparison of operating costs for a new open-top vapor degreaser (OTVD), closed-loop degreaser, recovery system and a closed-loop system fitted with the co-solvent recovery system is displayed in Figure 7.

Table 12: Capital Cost Analysis for a Co-Solvent Recovery System

<u>SEPARATION EQUIPMENT</u>	<u>COST</u>
<u>BATCH DISTILLATION TANK</u>	
Batch distillation tank feed pump	\$400.00
Batch distillation tank, 3.5 ft dia.x 3.5 ft SS	\$4,667.52
Batch distillation tank insulation	\$1,526.66
Batch distillation tank condenser, 24 sqft	\$700.00
Batch distillation tank condenser insulation	\$37.47
<u>IPA RECOVERY COLUMN</u>	
Column plus auxiliaries, 16 stage, 36 in dia.	\$36,209.60
Column reboiler, 4 ft dia x 4 ft SS	\$5,094.90
Column reboiler insulation	\$1,930.78
Column transfer pump, 1-1/2 diaphragm	\$810.61
Column boiling heat exchanger, 35.2 sqft	\$800.00
Column condenser	\$3,200.00
Column condenser insulation	\$214.13
Column knock out pot, 30 gal capacity w/ feet	\$264.00
Column decanter, 30 gal capacity w/ feet	\$264.00
<u>NPB RECOVERY COLUMN</u>	
Column plus auxiliaries, 12 stage, 18 in dia.	\$14,347.20
Column reboiler, 3 ft dia x 3 ft SS	\$3,296.00
Column reboiler insulation	\$1,123.59
Column condenser	\$1,700.00
Column condenser insulation	\$118.26
Column knock out pot, 12 gal capacity w/ feet	\$224.00
Column decanter, 12 gal capacity w/ feet	\$224.00
CONTROL VALVES, ELECTRICAL AND CONTROLS, PIPING MATERIALS	\$65,758.00
 TOTAL CAPITAL INVESTMENT	 \$142,910.71

Table 13: Installation Costs for a Co-Solvent Recovery System

ITEM TO BE INSTALLED	COST
<u>BATCH DISTILLATION TANK</u>	
Batch distillation tank feed pump	\$80.00
Batch distillation tank, 3.5 ft dia.x 3.5 ft SS	\$160.00
Batch distillation tank insulation	included in material cost
Batch distillation tank condenser, 24 sqft	\$160.00
Batch distillation tank condenser insulation	included in material cost
<u>IPA COLUMN</u>	
Column plus auxiliaries, 16 stage, 36 in dia.	\$1,200.00
Column reboiler, 4 ft dia x 4 ft SS	\$160.00
Column reboiler insulation	included in material cost
Column transfer pump, 1-1/2 diaphragm	\$80.00
Column boiling heat exchanger, 35.2 sqft	\$160.00
Column condenser	\$160.00
Column condenser insulation	included in material cost
Column knock out pot, 30 gal w/ feet	\$80.00
Column decanter, 30 gal capacity w/ feet	\$80.00
<u>NPB COLUMN</u>	
Column plus auxiliaries, 12 stage, 18 in dia.	\$1,000.00
Column reboiler, 3 ft dia x 3 ft SS	\$160.00
Column reboiler insulation	included in material cost
Column condenser	\$160.00
Column condenser insulation	included in material cost
Column knock out pot, 12 gal w/ feet	\$80.00
Column decanter, 12 gal capacity w/ feet	\$80.00
CONTROL VALVES, ELECTRICAL AND CONTROLS, PIPING MATERIALS	\$4,400.00
TOTAL INSTALLATION COSTS	\$8,200.00

Operating costs were based on single shift, one-year operation. It is clear from Fig. 7 that the closed-loop system by itself has the lowest operating costs. However, this cost is based on single contaminant cleaning. Values for the OTVD and the closed-loop systems shown in Fig. 7 were determined from a cost comparison model (Gray, 2000). Costs for the co-solvent recovery system were computed from an extrapolated cost comparison model for miscellaneous items, current pricing from solvent distributors and waste management companies. The utility costs for the co-solvent recovery system are given in detail in Finger (2001).

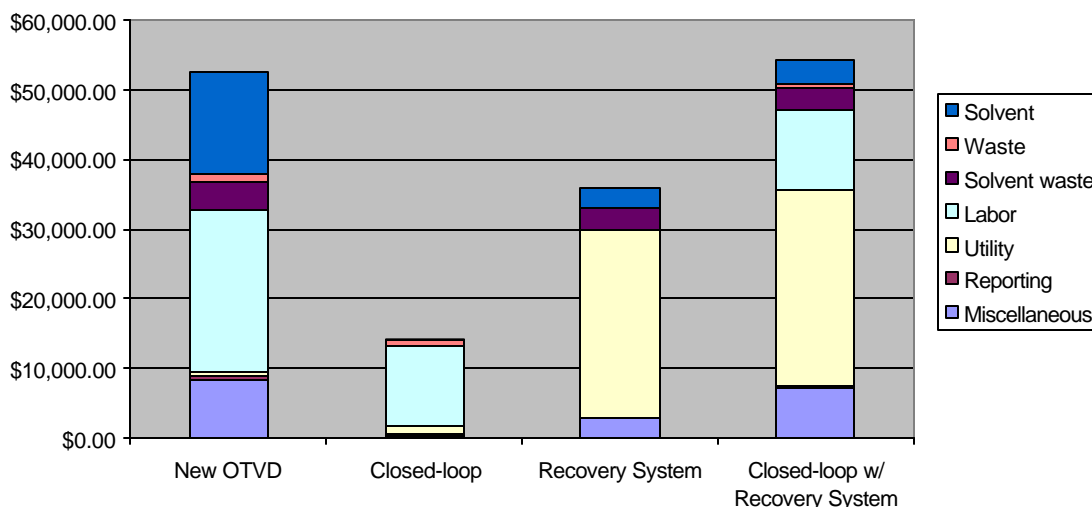


Figure 7: Operating Cost Comparison for Various Cleaning/Co-Solvent Recovery Systems

The closed-loop system fitted with the co-solvent recovery system is slightly higher in operating cost than the OTVD but is an attractive option when also considering the environmental impact of both systems. The OTVD emissions alone for a single shift operation for one year of operation exceed 3000 lbs compared to the closed-loop system of 200 lbs or less (Gray, 2000). Also, OTVD systems often violate one time exposure limits set forth by OHSA.

An additional point to consider is the fact that capital and operating costs for the co-solvent recovery system were based on maximum solvent recovery (highest purity). For acceptable purity levels lower than the values presented in section 6.1, the capital and operation costs will drop substantially, making the closed-loop system fitted with the co-solvent recovery system a more attractive economical option.

7. Conclusions. In this study, a method for solvent selection for industrial cleaning was proposed, analyzed and applied to co-solvent selection for multiple contaminant systems. A thermodynamic modeling framework for solvent selection using the binary Gibbs free energy of mixing was developed and compared to more traditional methods of solvent selection using Kauri-Butanol numbers and solubility parameters. Results clearly showed that binary Gibbs free energy of mixing with activity coefficients generated by the NRTL method provide a reliable and accurate method for solvent selection. A mixture of NPB-IPA was selected as a representative co-solvent mixture for removing organic-inorganic contaminants and was shown to be suitable

for cleaning oil-water emulsions from machined metal parts. Co-solvent cleaning often results in challenging solvent recovery, particularly if one or more of the contaminants are volatile to any appreciable extent. A co-solvent recovery system was synthesized, designed and analyzed both technically and economically. This study showed that co-solvent recovery is both cost-effective and environmentally responsible.

Finally, we close by noting that the binary Gibbs energy analysis presented in this paper is quite general and has widespread application, not only in the area of solvent selection for cleaning, but also for other applications in which some measure of relative solubilities is needed for decision-making. Clearly the need for environmentally friendly solvents abound in the chemical process, pharmaceutical and food industries. However, non-traditional needs for relative solubilities also exist. For example, Lucia et al. (2000) use binary Gibbs energy curves similar to those presented in this paper in conjunction with a variety of activity coefficient and equation of state models to determine all miscible and immiscible binary pairs and component distributions in multicomponent phase split and flash calculations. This strategy has been remarkably successful at providing good initial estimates of phase compositions and contributed significantly to the overall reliability of the multiphase flash algorithm described in Lucia et al. (2000) which is currently used within the Aspen Plus simulator.

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