PROCESS OPTIMIZATION AND INTEGRATION STRATEGIES FOR MATERIAL RECLAMATION AND RECOVERY

A Dissertation

by

HOUSSEIN A. KHEIREDDINE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

May 2012

Major Subject: Chemical Engineering

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Approved by:

Co-Chairs of Committee,	Mahmoud El-Halwagi
	Nimir Elbashir
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ABSTRACT

Process Optimization and Integration Strategies for
Material Reclamation and Recovery. (May 2012)

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Industrial facilities are characterized by the significant usage of natural resources and the massive discharge of waste materials. An effective strategy towards the sustainability of industrial processes is the conservation of natural resources through waste reclamation and recycles. Because of the numerous number of design alternatives, systematic procedures must be developed for the effective synthesis and screening of reclamation and recycle options. The objective of this work is to develop systematic and generally applicable procedures for the synthesis, design, and optimization of resource conservation networks. Focus is given to two important applications: material utilities (with water as an example) and spent products (with lube oil as an example). Traditionally, most of the previous research efforts in the area of designing direct-recycle water networks have considered the chemical composition as the basis for process constraints. However, there are many design problems that are not component-based; instead, they are property-based (e.g., pH, density, viscosity, chemical oxygen demand (COD), basic oxygen demand (BOD), toxicity). Additionally, thermal constraints (e.g., stream temperature) may be required to identify acceptable recycles. In this work, a novel approach is introduced to design material-utility (e.g., water) recycle networks that allows the simultaneous consideration of mass, thermal, and property constraints. Furthermore, the devised approach accounts for the heat of mixing and for the interdependence of properties. An optimization formulation is developed to embed all potential configurations of interest and to model the mass, thermal, and property characteristics of the targeted streams and units. Solution strategies are developed to identify stream allocation and targets for minimum fresh usage and waste discharge. A case study on water management is solved to illustrate the concept of the proposed approach and its computational aspects.

Next, a systematic approach is developed for the selection of solvents, solvent blends, and system design in in extraction-based reclamation processes of spent lube oil Property-integration tools are employed for the systematic screening of solvents and solvent blends. The proposed approach identifies the main physical properties that influence solvent(s) performance in extracting additives and contaminants from used lubricating oils (i.e. solubility parameter (δ), viscosity (υ), and vapor pressure (p)). The results of the theoretical approach are validated through comparison with experimental data for single solvents and for solvent blends. Next, an optimization formulation is developed and solved to identify system design and extraction solvent(s) by including techno-economic criteria. Two case studies are solved for identification of feasible blends and for the cost optimization of the system.

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1 INTRODUCTION TO PROCESS OPTIMIZATION AND INTEGRATION

1.1 Preface and Motivation

Mass, heat, and property integration have been used commonly in the industry in order to achieve core objectives of any process. Process integration has been used mainly for resource conservation, emission reduction, and sustainability performance improvement. These objectives have been targeted for decades now. However, they are more important than ever before due to:

- *The escalation of raw material prices*: Natural Gas, crude oil, and utilities such as fresh water and hydrogen prices keep increasing year after year. Energy is no longer cheap. Regardless of the political influence on these prices, optimization and integration of existing processes and invention of newer ones can help reduce and conserve these resources.
- *Depletion of natural resources*: processing facilities use tremendous amount of fresh materials. Such usage can lead to depletion of natural resources if not recycled and managed properly.

This dissertation follows the style of Education for Chemical Engineers Journal.

- *The irresponsible usage of utilities*: This applies especially to fresh water. It is a major factor in the lack of fresh water in major parts of the world. Dumping waste water stream irresponsibly back to the sea or into water ways has caused major environmental issues.
- *Increasing environmental regulations*: Environmental Protection Agency has been a major policy maker toward reduction of emissions and increase safety applications. Advances in technology and science allowed scientist better understand the effect of pollution on the environment and the human being. A lot of work could be done in that matter in order to help create safer world.

1.2 Key Strategies

1. Recycle and reuse: Not only from economic stand point, but recycling waste streams can have a major contribution to the conservation of these precious resources.

2. Process Modification/alteration: Addition of extra units to the process that helps purify toxic emissions is one way to help improve environmental performance and conserve natural resources. Another way is to change the process as a whole and reduce total utility usage while reaching the same output product.

3. Material substitution: Substitute toxic and unrecyclable resources by safer and recyclable alternatives.

1.3 Process Integration Introduction

Process integration is a holistic approach to process design, retrofitting, and operation whichemphasizes the unity of the process (El-Halwagi, 1997). It involves five main activities (El-Halwagi, 2006):

1. *Task Identification:* It is the expression of the goal that we are aiming for, and its description in actionable task.
2. *Targeting:* It is a very powerful tool that allows us to benchmark process performance without specifying the means of achieving these targets.
3. *Generation of Alternatives:* It is the generation of enormous number of possible solutions and configurations in order to achieve the goal/target.
4. *Selection of Alternative(s):* It is necessary to choose a feasible alternative. However, it is more important to choose an optimum one.
5. *Analysis of Selected Alternative(s):* It is important to evaluate the selected alternative. This evaluation may include economic analysis, safety analysis and assessment, etc.

1.3.1 Mass Integration

Mass Integration is a holistic approach to the generation, separation, and routing of species and streams throughout the process (El-Halwagi, 1997). It requires full understanding of the mass flow within the process (Figure 1.1). This mass integration could be done with the use of mass interceptors for purification purposes or it could be done without the purchase of any pieces of equipment (Direct Recycle). A source is a process stream that contains our target specie, and a sink is a process unit/equipment that can accept a source (El-Halwagi, 2006)

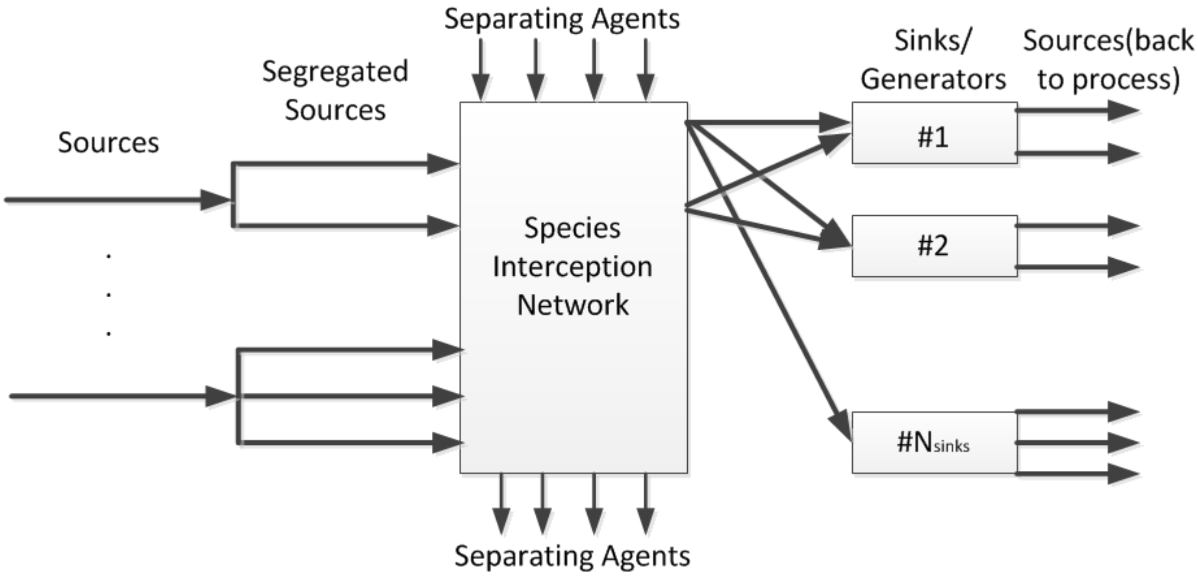

Figure 1.1: Mass integration schematic representation (El-Halwagi, Et Al 1996, Garrison Et Al 1996)

Over the past two decades a huge amount of effort has been done on development of mass integration strategies. Pinch analysis and mathematical programming methods were developed for targeting.

For example, Pinch analysis is a graphical method that targets minimum fresh materials, minimum waste discharged and maximum allowable recycle. The steps are as follow: 1, rank the sources and sinks in ascending order of compositions. Note that a common mistake is to rank them in ascending order of mass load. 2, In order to form the source and sink composite curve, plot the source and sink with the load of impurity versus flowrate. Each source is connected from the arrow of the previous source with superposition arrow starting from the sink with lowest composition. The same applies to sinks. After that, the source composite curve could be moved horizontally until touched by the sink composite curve. The point of intersection between the sink and source composite curves called the pinch point (Figure 1.2). The mass transfer flows from the process source to the sink upward on the graph. The flowrate that could not be transferred upward from a process source to process sink will be considered waste, and the flowrate that could not be supplied by a process source to a process sink upward, it will be supplied by a fresh source The thumb rule applied here is that, there should be no fresh feed to sink above the pinch, no waste from the source below the pinch, and no flowrate passed in the pinch (El-Halwagi, 2006).

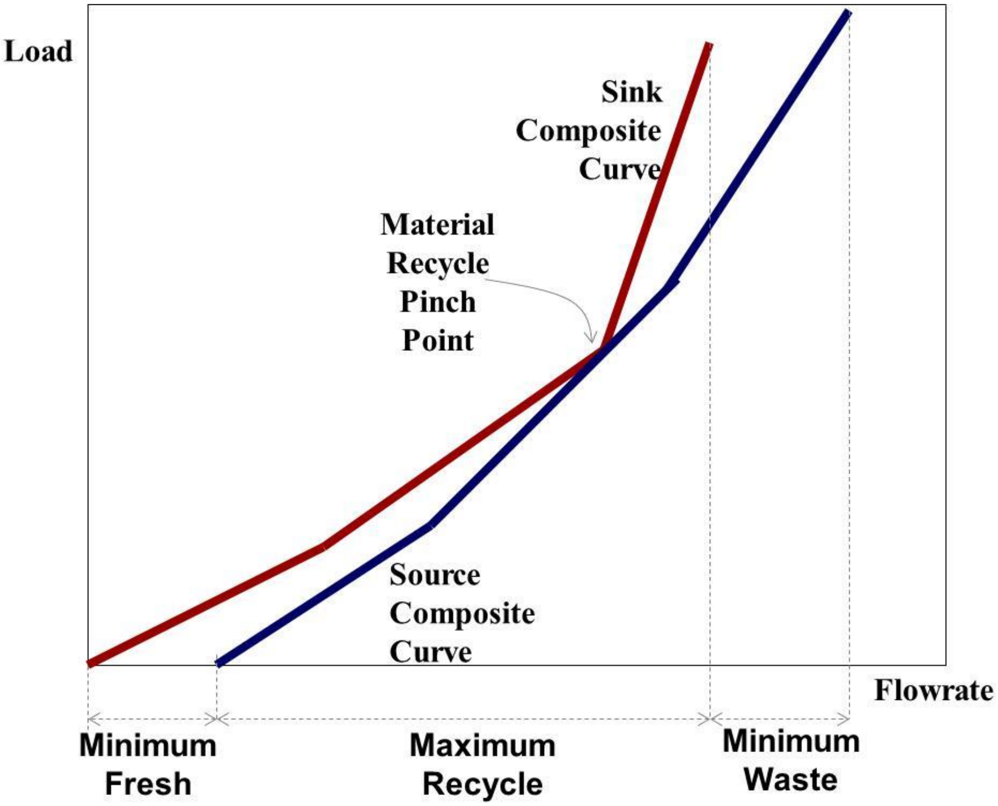

Figure 1.2: Sink and source composite diagram for material recycle pinch analysis (El-Halwagi, 2006)

Note that these targets are not theoretical, and they are achievable by following the correct procedures.

The mathematical programming model includes economic assessment of the process where The objective is to decide the minimum cost for the system, including the cost of the interceptors and the cost of the fresh feed cost and waste cost (El-Halwagi, 2006).

$$\text{Minimize total annualized cost} = C_{Fresh} \sum_{j=1}^{N_{sinks}} Fresh_j + \sum_{u=1}^{NU_{int}} C_u \times \alpha_u \times w_u \times y_u^{in} + C_{waste} \times waste \tag{1}$$

Subject to the number of constraints:

splitting of sources to all interceptores could be expressed as follow:

$$F_i = \sum_{u \in U_i} w_u \quad i = 1,2, \dots N_{sinks} \tag{2}$$

For purification purposes, the removal of pollutant in uth interceptor is:

$$y_u^{out} = (1 - \alpha_u) \times y_u^{in} \quad u = 1,2, \dots NU \tag{3}$$

After interception, the source split could be presented in equation (1.4):

$$w_u = \sum_{u=1}^{NU} g_{u,j} \; + g_{u,waste} \quad u = 1, \dots NU \tag{4}$$

The mass balance around sink j at the feed mixing point can be shown as follow:

$$G_j = Fresh_j + \sum_{u=1}^{NU} g_{u,j} \quad j = 1, \dots N_{sinks} \tag{5}$$

Component Material balance for each sink j when mixing is expresses below:

$$G_j \times z_j^{in} = Fresh_j \times y_{fresh} + \sum_{u=1}^{NU} g_{u,j} \times y_u^{out} \quad j = 1,2, \dots N_{sinks} \tag{6}$$

Sink j material composition upper and lower bounds can be presented as follow:

$$z_j^{min} \le z_j^{in} \le z_j^{max} \quad j = 1,2, \dots N_{sinks} \tag{7}$$

All the process flows that could not be allocated to a process sink will be sent to waste:

$$waste = \sum_{u=1}^{NU} g_{u,j,waste} \tag{8}$$

where

α_u is the separation efficiency of the interceptor u

C_u is the cost of the interceptor u

C_{Fresh} is the fresh feed cost

C_{waste} is the waste treatment cost

$Fresh$ is the flowrate of fresh feed

$waste$ is the flowrate of waste stream

y_u^{in} is the composition from each source to unit u

w_u is the flowrate to each unit u

$g_{u,j}$ is the flowrate coming out of each unit u to different sink j

G_j is the flowrate into each sink j

F_i is the flowrate of each source i

z_j^{in} is the composition of streams into each sink j

1.3.2 Property Integration

Mass integration is very powerful targeting tools. It was to batch and continuous water networks. However, a major feature of mass integration is that it is chemo-centric. This means that the chemical composition of a stream is the only parameter being tracked. Because of the heavy dependence of the system design on properties, a more important approach for optimal design is the framework of property integration which is defined by El-Halwagi et al. (2004) as "a functionality-based holistic approach for the allocation and manipulation of streams and processing units, which is based on functionality tracking, adjustment and assignment throughout the process." Several graphical and algebraic techniques have been developed for designing and optimizing recycle/reuse systems based on property integration (e.g., Shelley and El-Halwagi,2000; El-Halwagi et al.,2004; Qin et al.,2004; and Ng et al.,2009).

This dependency of the system design on properties poses major property constraints. The identification of the upper and lower property bounds values are not as simple as they sound. They could be extracted from experimental results or via simulation runs. This could be presented as following:

$$p_i^{\min} \leq p_i \leq p_i^{\max} \tag{9}$$

One of the major challenges of property integration is the identification of the mixing rule expression. Different properties can have different mixing rules. Some may be linear, and others can be non-linear. A generic mixing rule expression is shown below (El-Halwagi, 2004):

$$\bar{F} \times \psi(\bar{P}) = \sum_i F_i \times \psi_r(p_i) \tag{10}$$

with,

$\bar{P}$ is the property of the mixture

$\psi(P_i)$ is the property mixing operator of property r

$\bar{F}$ is the flowrate of mixture and can be expressed as follow:

$$\bar{F} = \sum_i F_i \tag{11}$$

Note that the multiplication of the flowrate by the property operator is considered the property load. Thus, composition can be considered as a special case of property, and the same mass integration pinch analysis that was applied to mass can be applied to any property. This is very important when it comes to the allocation of process sources and sinks taking into account composition and property constraints.

In order to normalize the property operator into a dimensionless operator Ω, its division by a reference value $\psi_i^{ref.}$ is needed:

$$\Omega_{r,i} = \frac{\psi_r(p_{r,i})}{\psi_r^{ref}} \tag{12}$$

Then, an AUgmented Property (AUP) index for each stream i is the summation of the dimensionless operators:

$$AUP_i = \sum_{r=1} \Omega_{r,i} \tag{13}$$

Then, the cluster for property r in stream i can be defined as follow:

$$C_{r,i} = \frac{\Omega_{r,i}}{AUP_i} \tag{14}$$

Now, through clustering, every stream can be presented in a ternary diagram by a single point. This could be illustrated in figure 1.3. A very important characteristic of clustering is that the summation of clusters is equal to 1.

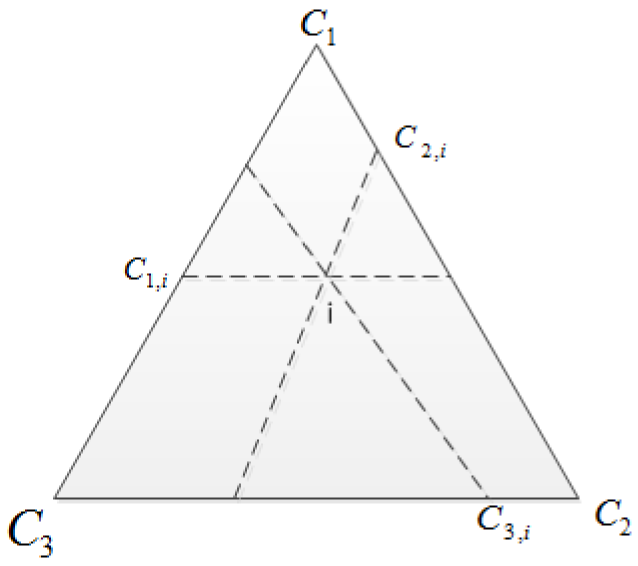

Figure 1.3: Ternary diagram representation of Intra-Stream of clusters (Shelly and El-Halwagi, 2000)

Another important characteristic of clustering is that it is consistent with lever-arm additive rule. This means that the resulting mixing stream lies on the line that connects both points in the ternary diagram. This could be illustrated in figure 1.4.

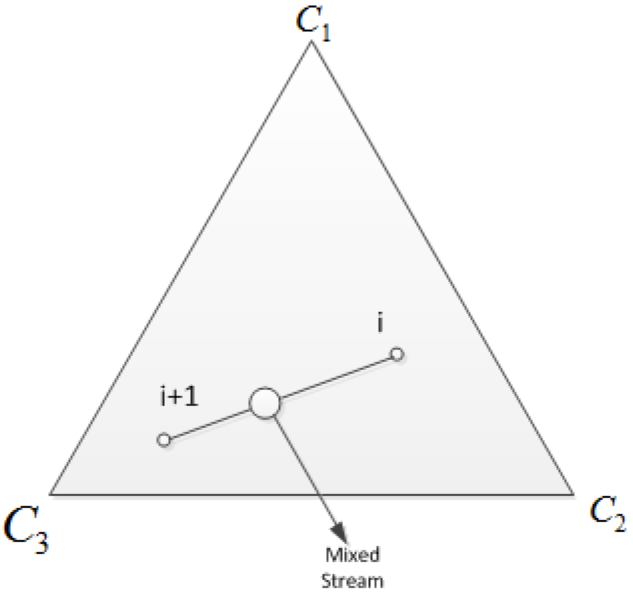

Figure 1.4: Lever arm addition for clusters (Shelly and El-Halwagi, 2000)

1.4 Optimization

Optimization is the recognition of the best solution among all available alternatives (El-Halwagi, 2006). The main objective of an optimization formulation is to maximize or minimize an objective function. This objective function is usually subject to a number of constraints. These constraints could be linear or non-linear. The more the non-linear constraints are present in the formulation, the more complex it gets to find the optimal solution. Also, the variables could be decimals or integers. A special case of integer variable is the binary integers where the variable could be only hold a value of zero or one. Otherwise, it will be called mixed integer variable.

The mathematical formulation of an optimization model entails the following steps (El-Halwagi, 2006):

1- *Determine the objective function:*
  - Identify the quantity/value that needs to be maximized or minimize (maximize profit or minimize cost)
  - Identify the variables that should be included in the function
  - Express the objective function mathematically

2- *Develop the game plan to tackle the problem:*
  - Identify how to address the problem
  - What is the validation, motivation, and reasoning
  - What are the key concepts that can help develop a formulation that reflects your input and thoughts

3- *Develop the constraints:*
  - Convert the approach to a mathematical framework
  - Determine mathematically all the relations and restrictions
  - Determine the region(s) where the solution can be accepted
  - Include subtle constraints

4- *Improve formulation:*
  - Avoid non-linearity
  - Simplify the formulation as much as possible
  - Enhance clarity for debugging purposes

1.5 Dissertation Goals

Water and used lubricating oil are the two waste streams that have been considered in this work. The mishandling of these two species has led to major industrial and environmental issues.

Process integration is an important tool that helped not only target water recycle and lube oil reclamation for resource conservation and environmental purposes, but it also made it economical to do so. This economical drive has posed an important task on industry decision makers to benchmark performance and make the modifications needed to reach those targets.

The following sections will reveal in details the objective of the proposed approach and how it contributes to the resource conservation and reclamation (Section 2). Then, a full description of the water direct recycle network problem statement is presented, and followed by the proposed approach. This is followed by case study in order to illustrate the applicability of the proposed approach (Section 3). Then, problem statement describing the need for a systematic approach for solvent selection in the re-refining of used lubricating oil is described. Then a validation of the proposed approach using experimental result is shown (Section 4). After forming a solvent consideration set using the proposed approach in section 4, an optimization formulation that maximizes profit is developed in section 5. This is done in order to obtain clear optimal results for solvent selection based on economic assessment.

Finally, a case study and sensitivity analysis is presented (Section 5). Finally, section 6 will include an overall conclusion and recommendations for future work.

2 OBJECTIVES OF WORK

2.1 Objectives Overview

Sustainability is the satisfaction of the present generation without depriving the future generation from the ability to meet their needs. It has social, economic, and environmental dimensions. Therefore, in order to operate in a sustainable matter, there is a need for efficient and responsible usage of natural resources. The intent here is to focus on the development of systematic and generally applicable tools for the design, integration, and optimization of resource-conservation networks that reduce the consumption of fresh natural resources and the discharge of waste materials to the environment. This focus is given to two important applications: water conservation and lube-oil reclamation. For water conservation, an optimization approach will be developed to enable the recycle of process streams while considering economic issues as well process requirements involving mass, thermal, and property constraints. Next, lube oil reclamation will be addressed to conserve the use of fresh base oil and to reduce the discharge of spent oil. Two approaches will be developed. The first one is intended to identify important bounds for the selection of solvents and solvent blends that can be effectively used in extracting the base oil and rejecting contaminants and sludge. The second approach involves the development of an optimization program that screens solvents and blends and optimizes process design for lube-oil reclamation.

2.2 Water Conservation and Direct Recycle Network

There is a growing need to develop systematic and cost-effective design strategies for direct recycle strategies that lead to the reduction in the consumption of fresh materials and in the discharge of waste streams. Direct recycle network is defined as the case when rerouting of waste streams does not require the purchase of any new pieces of equipment (El-Halwagi, 2006). These equipments are usually mass interceptor such as stripper, scrubber, etc. In that case, mass separating agents will be required to purify or modify the impurity composition. Traditionally, most of the previous research efforts in the area of designing direct-recycle networks have considered the chemical composition as the basis for process constraints. However, there are many design problems that are not component based, but they are property based (e.g., pH, density, viscosity, COD, BOD, toxicity). Additionally, thermal constraints (e.g., stream temperature) may be required to identify acceptable recycles. In this work, we introduce a novel approach to the design of recycle networks which allows the simultaneous consideration of mass, thermal, and property constraints. Furthermore, the devised approach also accounts for the heat of mixing and for the interdependence of properties. An optimization formulation is developed to embed all potential configurations of interest and to model the mass, thermal, and property characteristics of the targeted streams and units. Solution strategies are developed to identify stream allocation and targets for minimum fresh usage and waste discharge. A case study is solved to illustrate the concept of the proposed approach and its computational aspects.

2.3 Lube Oil Reclamation and Property Integration

2.3.1 Solvent Selection Systematic Approach

When thinking along the sustainability lines, one of the main areas that come to mind is lube oil reclamation. It is used for many different applications (refer to section 4). It is composed of base oil and additives. Because of its stability characteristic, the base oil molecules stay almost intact after usage. However, the man made additives wear out. The need for sustainable re-refining technique is necessary. Also, the significant quantities of used and discharged lubricating oils pose a major environmental problem around the world. Recently, there has been a growing interest in the sustainable usage of lubricating oils by adopting recovery, recycle, and reuse strategies. In this work, a property-integration framework is used in the optimization of solvent selection for re-refining of used lubricating oils. Property-integration tools are employed for the systematic screening of solvents and solvent blends. The proposed approach identifies the main physical properties that influence solvent(s) performance in extracting additives and contaminants from used lubricating oils (i.e. solubility parameter (δ), viscosity (υ), and vapor pressure (p)). To identify a feasibility region for an effective solvent or solvent blends for this process, we construct a ternary diagram utilizing the property-clustering technique. The results of the theoretical approach are validated through comparison with experimental data for single solvents and for solvent blends.

2.3.2 Optimization Formulation for Solvent Extraction in the Lube Oil Application

As discussed above, he lube oil reclamation is necessary. This could be done by different technologies. Section 4 briefly describes the advantages and disadvantages of each process. As shown in section 4, solvent extraction is ultimate option for many reasons. This could be done through the use of organic solvents. This recycling should not be done for environmental purposes only, but for economical drive as well. The selection of solvent is not an easy task. After the application of screening method proposed and justified in section 4, feasible solvent consideration set could be developed. However, the selection of optimal solvent should not be valued based on experimental performance only. Therefore, an optimization formulation based on maximizing profit was formulated. This formulation takes into account the capital cost as well as the operating cost associated with each solvent. A case study excluding the capital cost was addressed to compare two major single solvents MEK and Butanol. Experimental results and Aspen Plus Simulation were used to collect the data required. Butanol performs better from PSR point of view. MEK performs better from POL stand point. In most cases, MEK was favored due to its lower cost and higher ability to preserve our valuable base oil product. Finally sensitivity analysis was performed in order to give better insight on the results obtained.

3 OPTIMIZATION OF DIRECT RECYCLE NETWORKS WITH THE SIMULTANEOUS CONSIDERATION OF PROPERTY MASS AND THERMAL EFFECT

3.1 Introduction

The efficient use of natural resources is a key challenge to industrial facilities seeking to operate in a sustainable manner. One of the promising means to accomplish the sustainability objectives is material recovery and effective allocation of resources. Over the past two decades, significant progress has been made in developing systematic process integration techniques for conservation of mass. This effort in the field of mass integration has emerged as an effective technique to identify performance targets for the maximum extent of material recovery within individual processes (El-Halwagi, 1997, 1998, and 2006; Dunn et al., 2003). Direct recycle is recognized as an effective saving tool in reducing the consumption of raw materials, generation of industrial wastes, and cost. Much research has been performed to design cost-effective material (e.g., water, hydrogen, solvent) recycle networks. Recent surveys can be found in literature (Foo, 2009; Faria et al., 2010; Jezowski, 2010). Three general approaches have been developed: graphical (Wang et al., 2004; Dhole et al., 1996; Alves et al., 2002; Hallale, 2002; El-Halwagi et al., 2003), algebraic (Feng et al., 2007; Sorin et al., 1999; Manan et al., 2004; Foo et al., 2006), and mathematical programming (El-Halwagi et al., 1996; Savelski et al., 2003; Hernandez-Suarez, 2004).

Early mass integration methodologies were based on stream compositions. Nonetheless, there are many wastewater streams that are characterized by properties in addition to concentrations. These problems can be effectively addressed by the property-integration framework which is defined as “a functionality-based holistic approach for the allocation and manipulation of streams and processing units, which is based on functionality tracking, adjustment and assignment throughout the process”(El-Halwagi, 2004). Using the property-based approach, several methodologies have been developed for the design of recycle/reuse networks. These include graphical (Shelly and El-Halwagi, 2000; Kazantzi 2005), algebraic (Qin, 2004; Foo, 2006), and optimization techniques (Ng et al., 2009; Ng et al., 2010; Ponce Ortega et al., 2009; Ponce Ortega, 2010; Nápoles-Rivera et al., 2010).

This paper expands the scope of recycle/reuse network by introducing for the first time a systematic approach which accounts for the simultaneous consideration of mass, property and operating temperature constraints to satisfy a set of process and environmental regulations. The paper also addresses the dependence of properties on composition and temperature. The problem is formulated as a nonlinear programming NLP problem that minimizes the total annualized cost of the system while satisfying the process and environmental constraints.

3.2 **Problem Statement**

The problem can be expressed as follows. Given is a set of sinks with the constraints for the inlet flowrates and allowable compositions, properties and temperatures. Also given is a set of fresh and process sources, which can be recycle/reused in sinks. Each source has a known flowrate, composition, property and temperature. The fresh sources have to be purchased to supplement the use of process sources in sinks. In addition, the discharged waste has to meet the environmental regulations. The objective is to find an optimal direct recycle/reuse network while simultaneously considering property, mass, and thermal effects and minimizing the cost the overall system. Furthermore, the devised approach should also account for the heat of mixing and for the interdependence of properties.

3.3 **Approach and Mathematical Formulation**

A source-sink mapping diagram is used to represent the superstructure of the problem embedding potential configurations of interest (Figure 3.1). Each source is split into fractions that are mixed with fractions of other streams to form the feeds to the process sinks which must meet the process constraints expressed as bounds on concentrations, temperature, and properties.

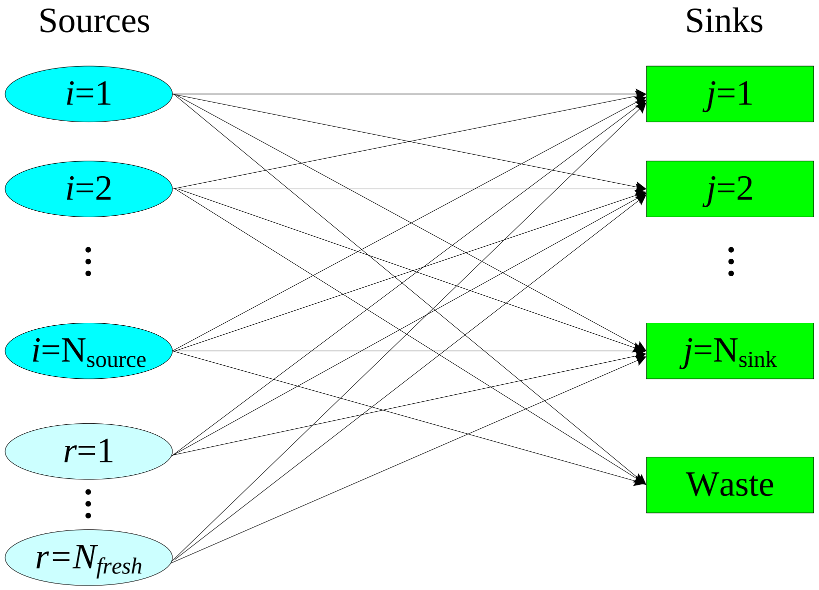

Figure 3.1: Source/sink allocation with direct reuse/recycle

Mass balance for the ith source:

$$F_i = \sum_{j \in NSINK} F_{i,j} + F_{i,waste} \qquad i \in NSOURCE \tag{1}$$

A similar mass balance can be applied for *r*th fresh source without assign any fresh to waste:

$$F_r = \sum_{j \in NSINK} F_{r,j} \qquad r \in NFRESH \tag{2}$$

Mass balance for *j*th sink:

$$F_j = \sum_{r \in NFRESH} F_{r,j} + \sum_{i \in NSOURCE} F_{i,j} \qquad j \in NSINK \tag{3}$$

Component material balance for *c*th component in *j*th sink:

$$F_j z_{j,c}^{in} = \sum_{r \in NFRESH} F_{r,j} z_{r,c} + \sum_{i \in NSOURCE} F_{i,j} z_{i,c} \qquad c \in NCOMP, j \in NSINK \tag{4}$$

It is worth noting that the component material balances should be limited to the key components upon which constraints are imposed or the ones that highly impact the heat of mixing.

If the heat effect of mixing is involved, the heat balance for the *j*th sink is rewritten as:

$$F_j Cp_j (T_j^{in} - T_0) = \sum_{r \in NFRESH} F_{r,j} Cp_r (T_r - T_0) + \sum_{i \in NSOURCE} F_{i,j} Cp_i (T_i - T_0) + F_j \Delta H_j^{mix} \qquad j \in NSINK \tag{5}$$

where Cp can be calculated as

$$Cp = \sum_c x_c Cp_c \qquad c \in NCOMP \tag{6}$$

where x_c denotes the mole fraction of component *c* and *Cp* for each component can be calculated by a temperature-dependent expression. For example, the following linearized equation may be used:

$$Cp_c = a_c + b_c T \qquad c \in NCOMP \tag{7}$$

The heat of mixing can be calculated as,

$$\Delta H^{mix} = -RT^2 \left[\frac{\partial \left(G^E / RT \right)}{\partial T} \right]_{P,x} \tag{8}$$

For the case study, the Wilson Equation (Wilson, 1964) is selected. For the case of binary systems:

$$\begin{aligned} \frac{G^E}{RT} &= -x_1 \ln(x_1 + x_2\Lambda_{12}) - x_2 \ln(x_2 + x_1\Lambda_{21}) \\ \ln\Lambda_{12} &= a_{12} + {b_{12}}/{T} \\ \ln\Lambda_{21} &= a_{21} + {b_{21}}/{T} \end{aligned} \tag{9a}$$

where x is the mole fraction, T is the absolute temperature, and Λ is used to represent the Wislon's equation parameters. For multi-component systems:

$$\ln\gamma_i = 1 - \ln\left(\sum_j A_{ij} * X_j\right) - \sum_j \frac{A_{ij} * X_j}{\sum_k (A_{jk} * X_k)} \tag{9b}$$

where γ is the activity coefficient and A_{ij} is given as a function of absolute temperature:

$$\ln Aij = aij + \frac{bij}{T} + \frac{cij}{lnT} + dijT + eij/T^2 \tag{9c}$$

Hence, Eq. 9 can be expressed as,

$$\Delta H^{mix} = -Rx_1x_2 \left(\frac{\Lambda_{12}b_{12}}{x_1 + x_2\Lambda_{12}} + \frac{\Lambda_{21}b_{21}}{x_2 + x_1\Lambda_{21}} \right) \tag{1}$$

Property balance for the *p*th property in the *j*th sink,

$$F_j\varphi_p(p_{j,p}^{in}) = \sum_{r\in FRESH} F_{r,j}\varphi_p(p_{r,p}) + \sum_{i\in NSOURCE} F_{i,j}\varphi_p(p_{i,p}) \quad p \in NPROP, j \in NSINK \tag{2}$$

Here the property is dependent on the temperature and other properties p', the operator can be considered as a function of temperature and other properties:

$$\varphi_p(p) = f(T, p') \qquad \forall p' \neq p \tag{3}$$

Sinks composition constraints:

$$z_{j,c}^{\min} \leq z_{j,c}^{in} \leq z_{j,c}^{\max} \qquad c \in NCOMP, j \in NSINK \tag{4}$$

Sinks temperature constraints:

$$T_j^{\min} \leq T_j^{in} \leq T_j^{\max} \qquad j \in NSINK \tag{5}$$

Sinks properties constraints:

$$p_{j,p}^{\min} \leq p_{j,p}^{in} \leq p_{j,p}^{\max} \qquad p \in NPROP, j \in NSINK \tag{6}$$

It is important to point out that one of the sinks is the environmental discharge system with Eqs. (13)-(15) correspond to the environmental regulations. Mass balance for the waste:

$$F_{waste} = \sum_{i \in NSOURCE} F_{i,waste} \tag{7}$$

The *c*th component load in the waste stream can be obtained through the following component mass balance:

$$F_{waste} z_c^{waste} = \sum_{i \in NSOURCE} F_{i,waste} z_{i,c} \qquad c \in NCOMP \tag{8}$$

Considering the heat effects of the mixing, the temperature for the waste can be calculated as:

$$F_{waste}Cp_{waste}(T_{waste}^{in}-T_0)=\sum_{i\in NSOURCE}F_{i,waste}Cp_i(T_i-T_0)+F_{waste}\Delta H_{waste}^{mix} \tag{9}$$

The *p*th property load in the waste stream is expressed through the following property mixing rule:

$$F_{waste}\varphi_p(p_{waste,p}^{in})=\sum_{i\in NSOURCE}F_{i,waste}\varphi_p(p_{i,p}) \qquad p\in NPROP \tag{10}$$

The objective function aims to minimize the total annualized cost, which involves the cost for the fresh sources, cost for the waste discharge, and cost for the pipeline.

$$\begin{aligned} TAC = &\sum_{r\in NFRESH}\mathrm{Cost}_r F_r H_Y + \mathrm{Cost}_{waste}F_{waste}H_Y \\ &+\sum_{\substack{r\in NFRESH\\ j\in NSINK}}\mathrm{pip}_{r,j}F_{r,j}+\sum_{\substack{i\in NSOURCE\\ j\in NSINK}}\mathrm{pip}_{i,j}F_{i,j} \end{aligned} \tag{11}$$

3.4 **Case Study**

Figure 3.2 shows a schematic representation of the phenol production process from cumene hydroperoxide (CHP). Cumene is fed into the reactor along with air and Na_2CO_3 (which works as a buffer solution). In the reactor, cumene is oxidized to CHP. The mixture of CHP and cumene is then sent to a washing operation to remove the excess of the buffer solution and water-soluble materials.

Next, the stream leaving the washer is sent to a concentration unit in order to increase the low concentration of CHP to 80 wt.% or higher. After that, the concentrated CHP stream is fed to the cleavage units where the CHP is decomposed to form phenol and acetone in the presence of sulfuric acid. The resulting cleavage stream is neutralized with a small amount of sodium hydroxide and then it is separated into two phases (organic and water phases). The water phase is sent to wastewater treatment and the organic phase (which is mainly a mixture of phenol, acetone and cumene) is washed with water to remove the excess alkali and is finally sent to distillation columns where it is fractionated into the pure products phenol and acetone. This could be simplified in a simple flow diagram (Figure 3.2) that summarizes visually the process described above.

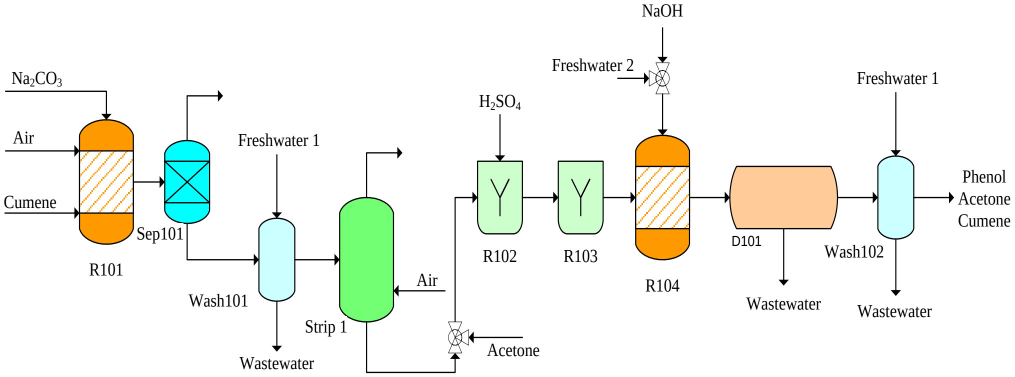

Figure 3.2: Process flowsheet of the production of phenol from cumene

3.4.1 Data Extraction (Scenario 1)

Phenol is chosen as the key pollutant due to its environmental hazards and carcinogenic effects. The property studied in this case study is the vapor pressure due to its significant contribution volatility which affects both safety and environmental impacts. The lower and upper bound constraints on vapor pressure guarantee the compliance with the operational conditions as well as the environmental regulations. The following mixing rules are used for the pH and the vapor pressure:

$$10^{pH} = \sum_i x_i 10^{pH_i} \tag{21}$$

$$p = \sum_i x_i p_i \tag{22}$$

where x_i is the fractional contribution of stream i.

Below is the list of sources, sinks, and available fresh water sources:

- **Process sinks:**
  1. Waterwash Cumene peroxidation section (Wash101)
  2. Neutralizer (R104)
  3. Waterwash cleavage section (Wash102)
- **Process sources:**
  1. Stream 8 from Wash101
  2. Stream 22 from Decanter (D101)
  3. Stream 25 from Wash102

- **Fresh water sources:**
    1. Freshwater1: 0 impurity concentration
    2. Freshwater2: 0.012 impurity concentration (mass fraction)

Next, the relevant data are gathered from a developed ASPEN Plus simulation. The data are tabulated in Tables 3.1 and 3.2 for the sources and the sink data:

Table 3.1 Sources and fresh water (scenario 1)

Source	Flowrate (kg/hr)	Impurity Concentration z_i (Mass Fraction)	Temperature T(℃)	Vapor pressure (kPa)	Cost ($/tonne)
Washer101	3,661	0.016	75	38	
Decanter101	1,766	0.024	65	25	
Washer102	1,485	0.220	40	7	
Freshwater1		0.000	25	3	1.32
Freshwater2		0.012	35	6	0.88

Table 3.2 Sink data and constraints (scenario 1)

Sinks	Water Flowrate (kg/hr)	Maximum Inlet Impurity Concentration (Mass Fraction) z_j^{max}	Minimum Temperature T(℃)	Maximum Temperature T(℃)	Minimum Vapor pressure (kPa)	Maximum Vapor pressure (kPa)
Wash101	2,718	0.013	60	80	20	47
Wash102	1,993	0.013	30	75	4	38
Neutralizer R104	1,127	0.1	25	65	3	25

Note that scenario 1 will be calculated with and without heat of mixing considerations.

3.4.2 Data Extraction (Scenario2)

This scenario is an extension of Scenario 1 with the consideration of pH in addition to the vapor pressure, the chemical components, and thermal effects. The lower and upper bound constraints guarantee the compliance with the operational conditions as well as the environmental regulations, and they are presented in tables 3.3 and 3.4.

Table 3.3 Sources and fresh water (scenario 2)

Source	Flowrate (kg/hr)	Impurity Concentration z_i (Mass Fraction)	Temperature T(℃)	Vapor pressure (kPa)	pH	Cost (10^{-3} $/kg)
Washer101	3,661	0.016	75	38	5.4	
Decanter101	1,766	0.024	65	25	5.1	
Washer102	1,485	0.220	40	7	4.8	
Freshwater1		0.000	25	3	7	1.32
Freshwater2		0.012	35	6	6.8	0.88

Table 3.4 Sink data and constraints (scenario 2)

Sinks	Water Flowrate (kg/hr)	Max. Inlet Impurity Concentration (Mass Fraction)	Min. T(℃)	Max. T(℃)	Min.Vapor pressure (kPa)	Max Vapor pressure (kPa)	Min. pH	Max pH
Wash101	2,718	0.013	60	80	20	47	4.5	7
Wash102	1,993	0.013	30	75	4	38	4	8
Neutralizer R104	1,127	0.1	25	65	3	25	4.5	7
Waste		0.15					5	9

3.5 Solution and Results

Next, the proposed methodology is applied. The optimization software LINGO 11.0 is used to solve the developed NLP model by the embedded Global Solver. The value of the objective function, which is the cost of fresh water, cost of piping, and the cost of waste treatment, is evaluated for each case. The amount of fresh water needed without the direct recycle strategy is 5,838 kg/hr. However, the amount of fresh needed for all four scenarios after direct recycle are summarized in tables 3.5 and 3.6 along with other major results. These optimal results are illustrated in Figures 3.3, 3.4, and 3.5. Note that the heats of mixing values were noticeable. However, since water is the material being recycled coupled with the large values of other terms in equation (5), there were no changes in the overall optimal source sink allocation. This may not be the case in other case studies.

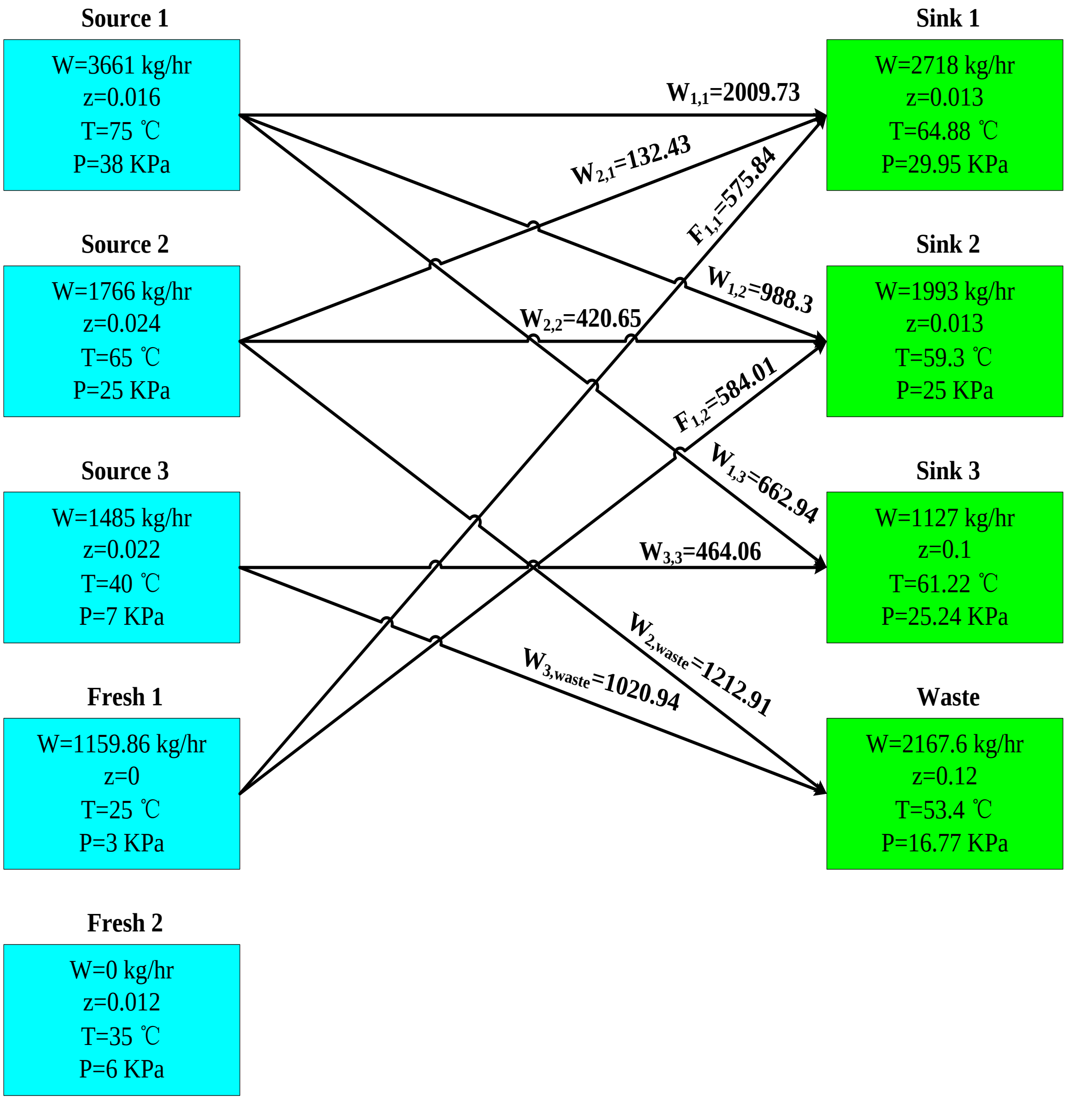

Figure 3.3: Optimal property-based water network with/without heat of mixing (scenario 1)

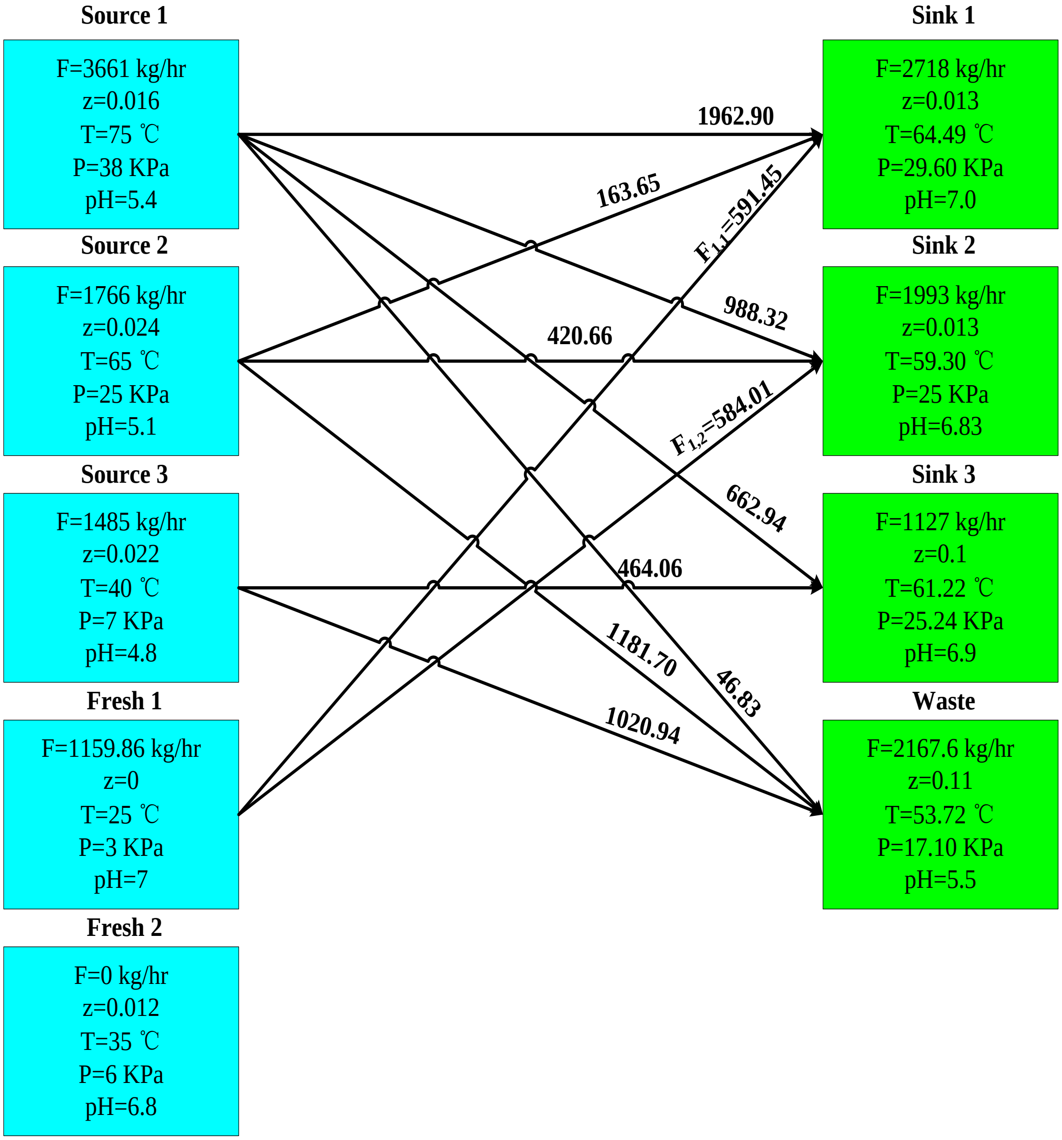

Figure 3.4: Optimal property-based water network with/without heat of mixing (scenario 2)

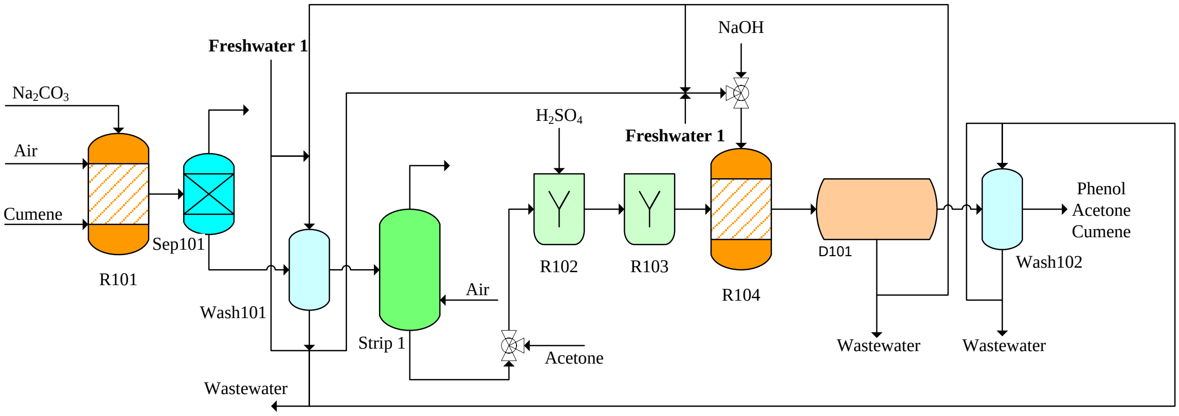

Figure 3.5 The retrofitted process flow sheet based on the optimized results

Table 3.5 Piping costs for the case study (32)

	Sources				
	Process, i			Fresh, r	
Sink, j	1	2	3	1	2
1	11.0231	4.4092	6.6138	9.9208	5.5115
2	7.7161	2.2046	11.0231	6.6138	2.2046
3	4.4092	8.8184	4.4092	7.7161	3.3069

*Units in [($·h)/(kg·year)]

Table 3.6 Comparison for the optimal results with/without property constraints

	NO PH	*PH*
Min Cost	93825	94016
$Fresh_1$(kg/hr)	1159.86	1175.47
$Fresh_2$(kg/hr)	0.00	0.00
$Fresh_{1,1}$(kg/hr)	575.84	591.45
$Fresh_{1,2}$(kg/hr)	584.01	584.01
$F_{1,1}$(kg/hr)	2009.73	1962.90
$F_{1,2}$(kg/hr)	988.33	988.33
$F_{1,3}$(kg/hr)	662.94	662.94
$F_{2,1}$(kg/hr)	132.43	163.65
$F_{2,2}$(kg/hr)	420.65	420.65
$F_{3,3}$(kg/hr)	464.06	464.06
$w_{1,waste}$ (kg/hr)	0.00	46.83
$w_{2,waste}$ (kg/hr)	1212.91	1181.70
$w_{3,waste}$ (kg/hr)	1020.94	1020.94
z_1	0.013	0.013
z_2	0.013	0.013
z_3	0.1	0.1
z_{waste}	0.11	0.11
T(sink1) (℃)	64.88	64.49
T(sink2) (℃)	59.30	59.30
T(sink3) (℃)	61.22	61.22
T(waste) (℃)	53.40	53.72
P(sink1) (kPa)	29.95	29.60
P(sink2) (kPa)	25.00	25.00
P(sink3) (kPa)	25.24	25.24
P(waste)	16.77	17.10
pH(sink1)	-	6.37
pH(sink2)	-	6.49
pH(sink3)	-	5.24
pH(waste)	-	5.00

3.6 Conclusions

This paper has introduced a systematic procedure which addresses for the first time the simultaneous handling of concentrations, temperature, and properties to characterize the process streams and constraints. This has been done taking into account the interdependency of properties and their dependency on concentrations and temperature. An optimization formulation has been developed to identify optimal allocation of sources to sinks that will minimize the network cost while satisfying all process and environmental constraints. Finally, a case study on water recycle in a phenol production plant is solved.

3.7 Nomenclatures

(i) Indices:

c=index for the components,

i=index for the internal sources,

j=index for the sinks,

p=index for the properties;

r=index for the fresh sources,

waste= index for waste;

(ii) Sets:

NCOMP={ c | c is one of the components},

NFRESH={r | r is a fresh source},

NPROP={p | p is one of the properties};

NSINK={j | j is an internal sink},

NSOURCE={i |i is an internal source},

(iii) Parameters:

a_c = Parameter in linerized temperature-dependent expression for heat capacity of the pure component, 1.3724 J/(g·K) for water, 0.4685 J/(g·K) for phenol,

b_c = Parameter in linerized temperature-dependent expression for heat capacity of the pure component, 0.0083 J/(g·K) for water, 0.0044 J/(g·K) for phenol,

a_{12} = Binary parameter in Wilson equation for phenol and water solution, 2.4395,

a_{21} = Binary parameter in Wilson equation for phenol and water solution, -3.2239,

b_{12} = Binary parameter in Wilson equation for phenol and water solution, -2229.9297 K,

b_{21} = Binary parameter in Wilson equation for phenol and water solution, 1046.1246 K,

Cp_c =heat capacity of the pure component,

Cp_i =heat capacity dependant on temperature of process source *i*,

Cp_r =heat capacity dependant on temperature of fresh source *r*,

Cost_r =unit cost of fresh source *r*,

Cost_{waste} = unit cost of *waste*;

F_i =total mass flowrate from process source *i*,

F_j =total mass flowrate inlet process sink *j*,

T_0 = reference temperature, assumed to be 0℃,

T_r =temperature of fresh source *r*,

T_i = temperature of process source *i*,

$T_j^{\min}$ =minimum temperature of process sink *j*,

$T_j^{\max}$ =maximum temperature of process sink *j*,

$p_{r,p}$ =*p*th property of fresh source *r*,

$p_{i,p}$ =*p*th property of process source *i*,

$p_{j,p}^{\min}$ =minimum property for *p*th property of process sink *j*,

$p_{j,p}^{\max}$ = maximum property for *p*th property of process sink *j*,

R = ideal gas constant, 8.314 J/(K·mol),

$z_{r,c}$ = composition for *c*th component of fresh source *r*,

$z_{i,c}$ = composition for *c*th component of process source *i*,

$z_{j,c}^{\min}$ =minimum composition for *c*th component of process sink *j*,

$z_{j,c}^{\max}$ =maximum composition for *c*th component of process sink *j*,

H_y =Annual operating hours =8000 hr/year

(iv) Variables:

Cp_j = heat capacity dependent on temperature of process sink *j*,

Cp_{waste} = heat capacity dependant on temperature of the waste,

F_r =total flowrate consumed from fresh source *r*,

$F_{r,j}$ =segregated mass flowrate from fresh source *r* to sink *j*,

F_{waste} =total mass flowrate of the waste,

$p_{j,p}^{in}$ = inlet property for *p*th property of process sink *j*,

$p_{waste,p}^{in}$ =inlet property for *p*th property of process waste,

T_j^{in} =inlet temperature of process sink *j*,

T_{waste}^{in} = inlet temperature of the waste,

$F_{i,j}$ =segregated mass flowrate from process source *i* to sink *j*,

$F_{i,waste}$ =segregated mass flowrate from process source *i* to the waste stream,

G^E = Excess Gibbs free energy, J/(K·mol),

z_c^w = composition for *c*th component of the waste *w*,

$z_{j,c}^{in}$ =inlet composition for *c*th component of process sink *j*,

ΔH_{waste}^{mix} =enthalpy change in the mixing node before the waste,

ΔH_j^{mix} =enthalpy change in the mixing node before process sink *j*,

$\varphi_p(p)$ =property operator of *p*th property,

Λ_{12} = Binary variable in Wilson equation for phenol and water solution,

Λ_{21} = Binary variable in Wilson equation for phenol and water solution,

4 A PROPERTY-INTEGRATION APPROACH TO SOLVENT SCREENING AND CONCEPTUAL DESIGN OF SOLVENT-EXTRACTION SYSTEMS FOR RECYCLING USED LUBRICATING OIL

4.1 Introduction and Literature Review

Lubricating (lube) oils are used in significant quantities to reduce friction between surfaces in moving parts. Lube oil primarily consists of base oil (85-90%) and additives (10-15%). The United States Department of Energy (DOE) reported the total national and global demand of lube oil to be 2.5 and 10.3 billion gallons per year, respectively. Base oil is a mixture of liquid hydrocarbon molecules that contain around 20-70 carbon atoms. Base oil may be derived from various sources with crude oil being the primary commercial source. In order to enhance the performance of lube oil, *additives* are mixed with the base oil. Table 4.1 provides a list of the most common additives used in the lube oil application.

Table 4.1: List of Common additives used in lubricating oils (Kopeliovich, 2011)

Common Additives	Example(s)
Friction modifiers	Graphite, Boron Nitride
Anti-Wear	Esters,Chlorinated Paraffins
Rust and Corrosion Inhibitors	Organic acids, Alkaline compounds
Anti-Oxidants	Alkyl sulfides, Hindered Phenols
Detergents	Phenolates, sulphonates
Dispersants	Hydrocarbon succinimides
Pour Point Desperssants	Co-polymers of polyalkyl methacrylates
Viscosity Index Improvers	Acrylate polymers
Anti-Foaming	Dimethylsilicones

Upon utilization, the disposal of the used lube oils poses a major environmental problem. In this work, the term "*used oil*" refers to used lubricating oils that are collected after usage in small engines, automotive engines, industrial machines, etc. Besides consuming the additives during use, lube oil also becomes contaminated as it conducts its basic functions. Despite contamination, most of the base-oil portion in the used oil is not worn out. In fact, the chemical composition of the base oil is typically preserved to a large extent due to the high stability of the heavy compounds contained in the base oil. One gallon of lube oil yields 0.7 gallon of re-refined oil. As indicated earlier, the major difference between fresh lube oil and used oil is the breakdown of the additives to form contaminants that will mix with other light and heavy contaminants from the interiors of the engine. Other sources of contamination in used oils are generated from wear metals and road dust since one of the functions of motor lube oil is to clean the interior of the engine. Water is another major form of contamination in used oils. During fuel combustion, water and carbon dioxide are the main byproducts that pass through the exhaust when the engine is hot. However, when the engine is cold, condensed water may reach the lube oil lines. Another source of contamination is the oxidation of aromatics present in the base oil via the reaction with oxygen present in air.

Because of the relatively high cost of re-refining, used oils are normally disposed of in landfills or illegally dumped in waterways making it an environmental hazard. In a number of applications, lube oil has been successfully recycled (Laird, 1982). DOE reported that only 17 percent of the recycled oil is being re-refined (DOE, 2006). Examples of recycle alternatives include use as a fuel substitute in furnaces or as an extending agent in road-paving asphalt. Re-refining is intended for recovery of base oil for reuse for the original purpose as lube oil. Because of the rising prices of hydrocarbon fuels as well as the depletion of natural resources coupled with the ever increasing environmental regulations, an economically profitable and environmentally friendly re-refining technology that recovers the valuable base oil is essential. There are three major re-refining technologies that have been employed industrially to treat used oils. One of the oldest technologies used to treat used oils is chemical re-refining which is based on acid (normally sulfuric acid) followed by clay treatment. The acid-clay process involves atmospheric distillation to remove water and light hydrocarbons. Then, the dry used oil is treated with 5-10% by volume sulfuric acid. The sludge dissolves in the solvent (sulfuric acid), and settles down at the bottom of the decanter. The sludge containing sulfuric acid is removed from the bottom, and the clean oil is decanted out from the top, where it undergoes a neutralization step with the clay. The main advantage of this process is its capability to produce high quality base oil in an economically attractive manner. However, the acidic sludge collected from this process is environmentally hazardous, even more than the used oil itself, and, thus, requires quite expensive disposal techniques.

The other re-refining technique is the physical re-refining which is based on distillation processes that involve atmospheric distillation as well as vacuum distillation and thin-film evaporation. Similar to chemical re-refining, the first step is an atmospherics distillation process to recover the water and light hydrocarbons contaminants. This step is followed by vacuum distillation and thin-film evaporation (10-30 mmHg) to recover additives and other contaminants. In the last stage, the recovered base oil goes through a hydrogenation step in a hydro reactor to completely saturate the oxidized hydrocarbons. It is noteworthy to mention that despite the high cost of this process, it is more environmentally friendly than the chemical re-refining. However, this process has many challenges. For instance, the recovered oil is not of a high quality and therefore requires additional treatment. Additionally, fouling inside the distillation equipment normally occurs due to carbon deposition. More importantly, in order for this approach to become economically attractive it requires a steady and large volume input. Yet, both chemical re-refining (acid-clay process) and physical re-refining have found their way to commercialization scale.

The third major re-refining technique for recovering used oils is the solvent extraction re-refining process. This is a particularly attractive cleaner technology since it is aimed at conserving natural resources and recovering (instead of destroying) the base oil. In the solvent extraction process, the used oil and solvent are mixed in appropriate proportions to assure miscibility of the base oil in the solvent and the rejection of additives. A demulsifier is also used to coagulate the additives and dispersed particles and enhance their aggregation and rejection as large particle (flakes) that can be separated from the liquid by either sedimentation or centrifugation. These solvents are referred to as extraction-flocculation solvents (Reis and Jeronimo, 1988). Figure 4.1 is a simplified schematic representation of the process followed by a brief description of the process.

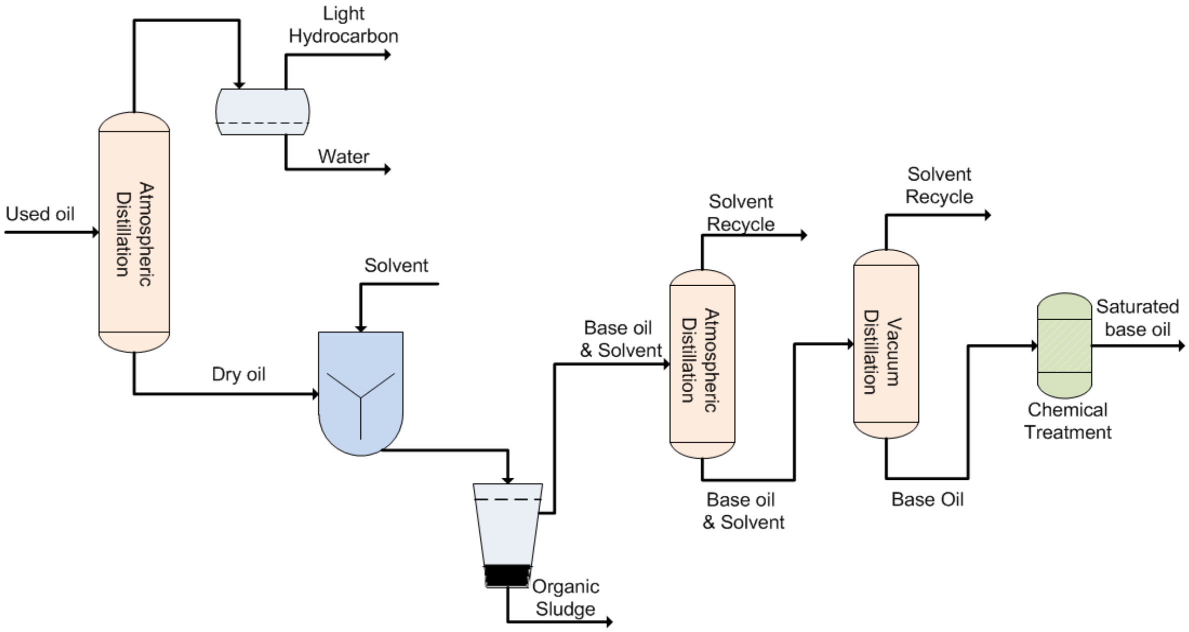

Figure 4.1: A simplified solvent extraction process.

In the first stage, the used oil is treated in an atmospheric distillation unit to remove water and light hydrocarbons. Then, the dry used oil is introduced to a mixer along with the solvent(s) in order to extract the base oil from the additives and heavy contaminants.

The mixing step is followed by a decantation unit whereby agglomeration and formation of large flakes take place and a two-phase solution is obtained. An organic sludge containing the worn additives and metals is decanted out the bottom of the decanter, and the top phase contains the base oil/solvent, which is separated and sent to a series of distillation columns for complete solvent separation for recycling purposes. Finally, base oil undergoes chemical treatment in order to adjust its physical properties and hydrocarbon structure to the required level. The major advantage of this technology is that it overcomes most of the limitations encountered by the aforementioned commercialized technologies. Compared to the acid-clay process, it produces a useful organic sludge that may be used in the asphalt or ink industries (Reis and Jeronimo, 1982). Also, it produces high quality base oil with less likelihood of fouling compared to the physical re-refining process. The process is also carried out at a lower overall operating cost for similar volume input

An important experimental measurement of the effectiveness of the solvent extraction re-refining process is normally represented by the amount of sludge removed from the used oil. This may be expressed as the ***percent sludge removal (PSR)***, which is the mass of sludge removed in grams per 100 g of oil (Reis and Jernimo, 1988). Another, important parameter is the ***percent oil losses (POL)***, which is the mass of base oil lost in the sludge phase expressed in grams per 100 g of oil (Reis and Jernimo 1988, and Elbashir et al. 2002). These two scales are key concepts in measuring the effectiveness of the solvent extraction process. The main operation parameters that control the efficiency of this process are temperature, solvent-to-oil ratio, and solvent type (normally referred to as the solvent extraction parameters or system). The characteristics of the required solvent for this process have been identified by Reis and Jernimo (1988) as follows: (1) it should be miscible in the base oil contained in the processed used oil; (2) should have the capability to reject additives and dispersed particle from the solvent-oil mixture; and (3) should be able to aggregate the remaining additives and contaminants to particle sizes large enough to be separated from the base oil and solvent mixture by either sedimentation, filtration, or centrifugation.

Despite the commercialization of numerous solvent extraction processes, there is still a need to design a systematic approach to quickly screen alternatives to identify a set of candidates that can be optimized. Such an approach has to; simultaneously identify appropriate solvent or solvent blends, design an efficient recovery process for the base oil, and establish a regeneration method for the recycle of the solvents, all while optimizing the overall cost of the process. Because of the system's dependence on solvent properties, a particularly well-suited approach for optimal design is the framework of *property integration* which is defined by El-Halwagi et al. (2004) as "a functionality-based holistic approach for the allocation and manipulation of streams and processing units, which is based on functionality tracking, adjustment and assignment throughout the process." Several graphical and algebraic techniques have been developed for designing and optimizing recycle/reuse systems based on property integration (e.g., Shelley and El-Halwagi, 2000; El-Halwagi et al.,2004; Qin et al.,2004; and Ng et al.,2009). Optimization techniques have been used to formulate recycle problems as property-integration tasks (e.g., Ponce-Ortega et al., 2009 and 2010, Ng et al., 2009; Nápoles-Rivera, 2010). Furthermore, a proposed model was used for the synthesis of property-based resource conservation networks in both batch and continuous process applications. The framework takes into account direct recycle network, interception, and waste treatment simultaneously (Chen, 2010). Combining process and molecular design has also been accomplished through process integration using group contributions methods (e.g., Chemmangattuvalappil et al., 2010; Solvason, 2009; Eljack et al.,2008 and 2007; and Kazantzi, 2007).

4.2 Problem Statement

Consider a solvent-extraction process for the recovery and reclamation of spent lube oil. The selection of proper solvents and blends is on the most important decisions for effective design and operation. It is desired to identify a systematic procedure to provide guidelines to the designer on selecting solvents and blends with proper properties. A combination of experimental data and simulation is to be used in defining the feasibility ranges for the desired properties. A property integration framework is to be utilized to generate bounds on the recommended solvents and blends.

4.2.1 Selection of Principal Properties and Construction of Property Clusters

While there are several successful experimental studies on the selection and design of solvent extraction systems for recycle of used lube oils, there is a need to develop systematic design approaches that guide the designer in selecting optimal solvents or solvent blends and designing the various components of the recovery system while accounting for the properties of the solvents, the properties of the used and recovered oil, and operational criteria such as percent sludge removal and percent oil losses (PSR and POL). The approach should also take into account the economic and environmental aspects of the design before determining an optimum. Additionally, it should cover every unit of the process starting from the atmospheric distillation up to the hydro treating step (see Figure 4.1). Different units may be impacted by different properties. For example, it is crucial to track the solubility parameter in solvent extraction applications, as it is important to track the specific gravity and relative volatility in decantation and distillation applications, respectively. Consequently, we chose the solubility parameter, viscosity, and vapor pressure as the major properties of concern for solvent selection. The following parameters are used in assessing the performance of the solvents and solvent blends:

-Solubility parameter: The latent heat of vaporization indicates the amount of van der Waals forces that hold liquid molecules together (Burk, 1984). For a solution to occur, the chosen solvent must overcome these forces and find their way around and between the base oil molecules. Solubility parameter is a good indicator of such a behavior. As it has been stated earlier, a good solvent for re-refining used oils must be highly miscible in the base oil and at the same time facilitate the miscibility of additives and their subsequent coagulation through the use of a demulsifier (Reis and Jernimo, 1988). These requirements have two indications in terms of solubility parameters of the three major components that form the used oil (base oil, solvent, and additives + contaminants). For dissolving the base oil and additives, the absolute value of the difference between solubility parameter of base oil and solvent has to be as close to zero as possible to facilitate the complete miscibility requirement. On the other hand, if the additives are completely miscible, it will be difficult to coagulate them into flakes using a demulsifer (such as KOH). Therefore, the absolute value of the difference between the solubility parameter of the solvent and base oil and additives has to be small enough for miscibility but not too small for coagulation and flocculation of the additives into separate flakes. An optimum range of solubility parameters of the solvent is needed. Another important factor is the polarity of the solvent which facilitates the rejection of the spent additives, impurities, carbonaceous particles to flocculate and form large flakes that settle under gravity action. Therefore, the optimum range of solubility parameters is selected for polar solvents (e.g. alcohols, ketones).

-***Viscosity:*** Lower viscosity solvents tend to function more favorably in solvent extraction processes. Higher viscosity solvents typically experience a greater amount of time for phase separation to occur. Also, the mass transfer resistance decreases as the viscosity of the solution decreases enabling higher solvent effectiveness. From an operational point of view, lower viscosity solutions are much easier to handle than higher ones (specifically on pumping and tube transportation) (King, 1971).

-***Vapor pressure:*** In order to complete the optimization loop, vapor pressure (e.g., Reid vapor pressure "RVP") must also be investigated. In order to obtain economical separation, the vapor pressure difference between the solvent and the base oil must be as great as possible so that the distillation process utilizes a minimum number of stages. While many solvents meet this criterion, there still must be a careful balance. Having too low of a vapor pressure causes the solvent to be very volatile whereby it is hard to accomplish appropriate mass transfer during the extraction process. Also, high volatility solvent may cause solvent losses due to atmospheric leaks causing environmentally hazardous problem and higher operation cost.

With the appropriate property parameters identified, it is possible to formulate a design using property-integration method. Here, we start with the concept of clustering. The ***Cluster*** terms were introduced by Shelley and El-Halwagi (2000) for componentless design and they have been used for the tracking of properties in the ***property integration*** framework proposed by El-Halwagi et al. (2004). From the above analysis, it can be concluded that there are constraints on the upper and lower bounds for each property; this can be expressed as follows (El-Halwagi, 2006):

$$p_i^{\min} \leq p_i \leq p_i^{\max} \tag{1}$$

where P is the property of interest that can either be the solubility, the viscosity, or the vapor pressure. The upper and lower bounds are determined either experimentally or via simulation. Mixing rules are used to track properties. For instance, the viscosity mixing rule may be expressed in the Arrhenius equation as follow:

$$\ln \bar{\upsilon} = \sum x_i \ln \upsilon_i \tag{2}$$

where,

x_i is the composition of pure component i in the mixture

$\bar{\upsilon}_i$ is the viscosity of pure component i in the mixture

$\bar{\upsilon}$ is the viscosity of the mixture

This means that the viscosity operator $\psi(\upsilon_i)$ can be expressed as follows (Shelley and El-Halwagi, 2000):

$$\psi(\upsilon_i) = \ln \upsilon_i \tag{3}$$

From equation (3), the viscosity dimensionless operator $\Omega_{\upsilon,i}$ can be determined using the following equation:

$$\Omega_{\upsilon,i} = \frac{\ln \upsilon_i}{\ln \upsilon_{ref}} \tag{4}$$

where,

υ_{ref} is the viscosity of a chosen reference solution

The Reid vapor pressure mixing rule can be expressed as follow:

$$\overline{F} * \overline{P}^{1.44} = \sum F_i * P_i^{1.44} \tag{5}$$

where,

$\overline{F}$ is the flowrate of the mixture

$\overline{P}$ is the Reid vapor pressure of the mixture

F_i is the flowrate of the pure component i in the mixture

P_i is the Reid vapor pressure of pure component i in the mixture

Therefore, the Reid vapor pressure operator $\psi(P_i)$ can be shown in equation (6). Then, the Reid vapor pressure dimensionless operator $\Omega_{p,i}$ is calculated using eqn. (7):

$$\psi(P_i) = P_i^{1.44} \tag{6}$$

$$\Omega_{p,i} = \frac{p_i^{1.44}}{p_{reference}^{1.44}} \tag{7}$$

where,

$p_{reference}$ is the Reid vapor pressure of a chosen reference solution.

The solubility mixing rule is linear and can be expressed in the following equation (Barton, 1991):

$$\overline{F} * \overline{\delta} = \sum F_i * \delta \tag{8}$$

where

$\overline{\delta}$ is the solubility parameter of the mixture

δ_i is the solubility parameter of the pure component i in the mixture

Therefore, the solubility operator $\psi(\delta_i)$ can be defined as follow:

$$\psi(\delta_i) = \delta_i \tag{9}$$

From equation (9), the solubility dimensionless operator can be calculated and expressed in the following equation:

$$\Omega_{\delta,i} = \frac{\delta_i}{\delta_{reference}} \tag{10}$$

where

$\delta_{reference}$ is the solubility parameter of a reference solution.

Then, the AUgmented Property index AUP_i introduced by Shelley and El-Halwagi (2000) is defined as the summation of the dimensionless operators as described below:

$$AUP_i = \sum_r \Omega_{r,i} \tag{11}$$

where r represents the properties being optimized. This approach also introduces a new parameter, which is the cluster of a property r, $C_{r,i}$, that is calculated as the fraction of the dimensionless operator divided by AUP_i:

$$C_{r,i} = \frac{\Omega_{r,i}}{AUP_i} \tag{12}$$

This can also be expanded to the following form to represent all properties of concern in this study:

$$C_{\upsilon,i} = \frac{\Omega_{\upsilon,i}}{AUP_i} \tag{13}$$

$$C_{P,i} = \frac{\Omega_{P,i}}{AUP_i} \tag{14}$$

$$C_{\delta,i} = \frac{\Omega_{\delta,i}}{AUP_i} \tag{15}$$

The sum of all the clusters as represented above is equal to one, i.e.:

$$\sum C_{r,i} = 1 \tag{16}$$

Therefore, on a ternary diagram for the clusters of vapor pressure, solubility, and viscosity, each solvent is represented by one point. Once the values of two clusters are determined, the third cluster is automatically determined (because the sum of clusters is one) as shown in Figure 4.2.

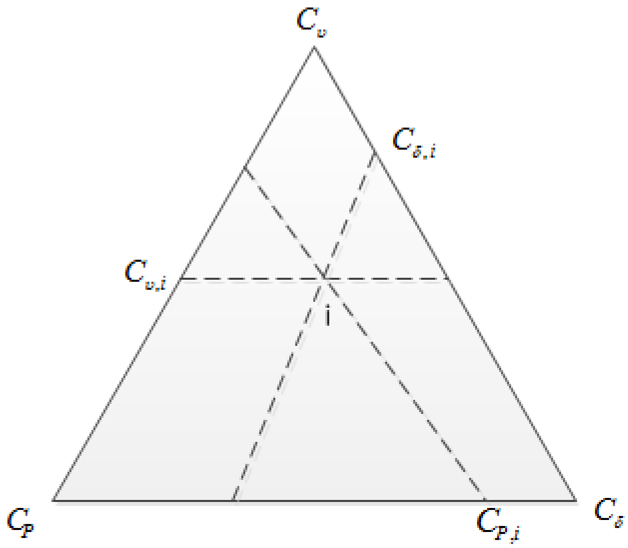

Figure 4.2: The ternary diagram for vapor pressure, solubility parameter, and viscosity

It is also worth noting that the constraints defining the feasibility region for any unit (such as the constraints described by Eq. 1) can be represented on the ternary diagram as shown by Figure 4.3. Based on the upper and lower bounds of each property, six points can be drawn on the ternary diagram. These points constitute the boundaries of the feasible region. When the sides of the feasibility region are extended, these lines pass through one of the three apexes of the ternary diagram. A feasible point (A) satisfying the constraints of a unit must lie inside the feasibility region of the unit. Furthermore, because lever arm rules apply for mixing, when two streams (B and C) are mixed, the resulting mixture (D) lies on the straight line connecting the two streams.

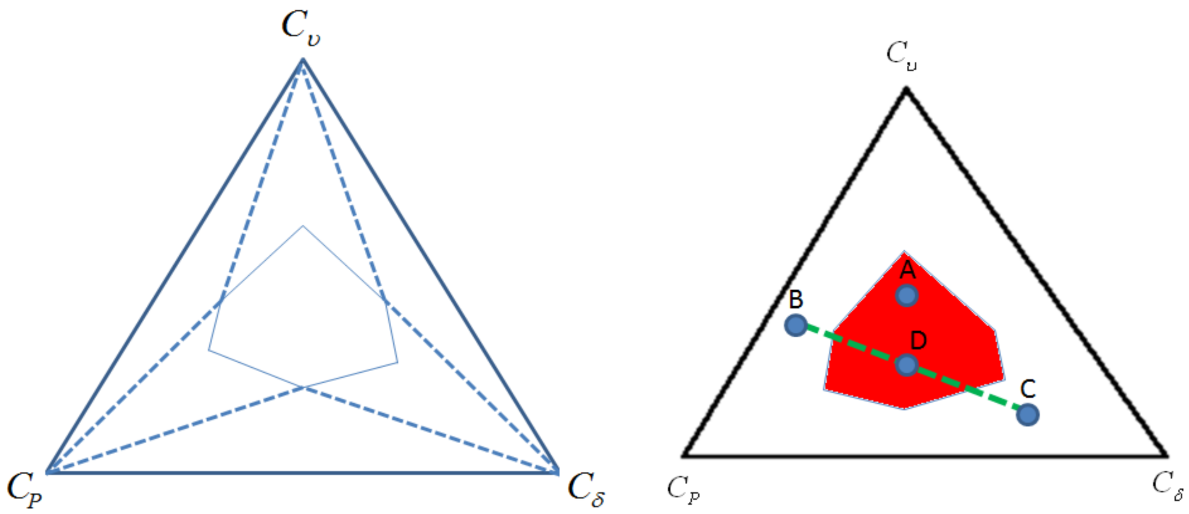

Figure 4.3: Ternary diagram that represents the three properties and identifies the feasible region for appropriate solvent extraction system

4.2.2 Design Approach

The proposed design approach is shown by the flowchart illustrated by Figure 4.3. It involves a combination of feasibility-region determination, property integration, and screening and optimization of feasible solvents and blends. The property constraints are used to construct the ternary cluster diagrams where the feasibility region is drawn and the candidate solvents are placed based on their properties. Solvents lying outside the cluster feasibility regions are discarded as infeasible but are still considered as candidates for blends. Straight-line segments connecting two solvents and passing through the feasibility region are potentially feasible (necessary but not sufficient condition). To insure feasibility, the values of the augmented properties (AUP) of the blends have to lie within the feasible range of properties. Based on the lever arms of the line segments lying within the feasibility region, the range of mixing ratios for blended solvents is determined. Cost data are used to screen the feasible solvents and blends. Whenever experimental data are available, they should be used to verify the design results, especially with regards to PSR and POL and the model results should be adjusted as needed. The result is a set of feasible solvents/blends along with system design arranged in order of cost. The design approach is presented if figure 4.4:

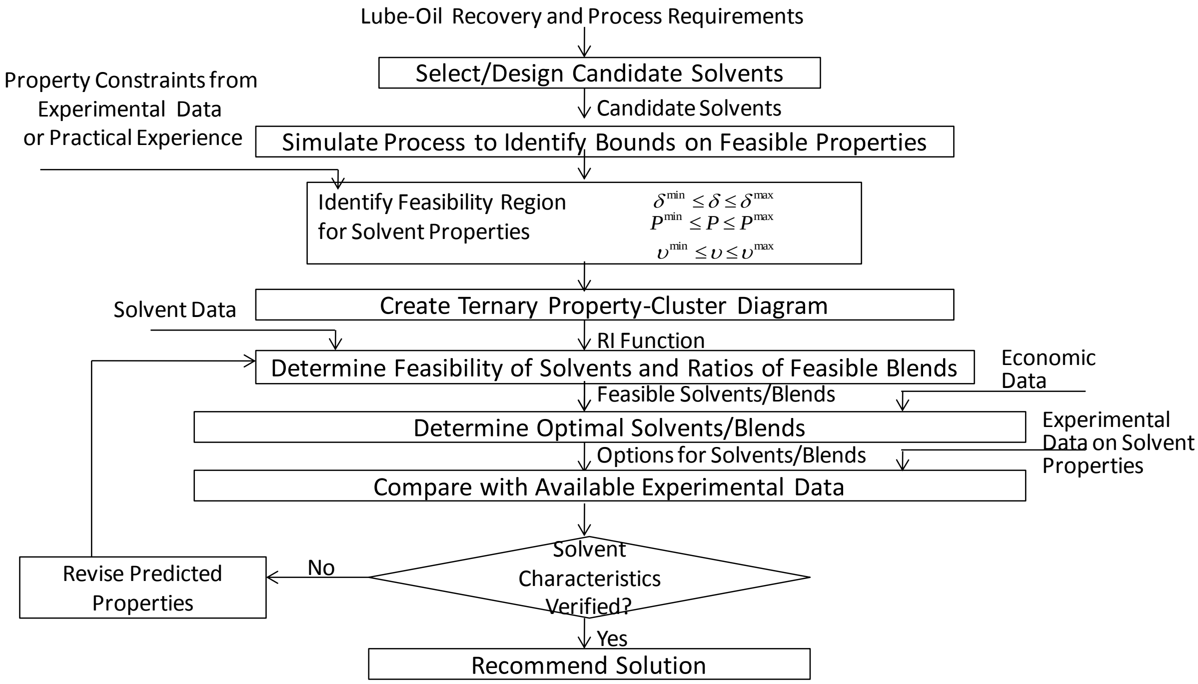

Figure 4.4: Schematic Diagram for our Solvent Design Approach

4.3 Case Study

In this section, three case studies are solved to demonstrate the applicability of the devised design approach. Before proceeding to the results of the case study, details are given on how the ranges of the three principal properties were determined.

a. Solubility Parameter:

Upper and lower bounds for the values of the Hildebrand solubility parameter have been determined through available experimental data. Table 4.2 lists the solubility parameters of major alcohols from C_1 to C_5 utilized in this process in addition to the solubility parameters of the base oil and typical chemicals used as additives (e.g. polyisobutylene as described by Elbashir, et al. 2002).

Table 4.2: Solubility parameters of base oil, additives and number of alcohol solvents

	δ (J/m3)^$^{1/2}$
Base oil	15.9
Additives	17
Methanol	29
Ethanol	26
Propanol	24.1
Butanol	22.5
Pentanol	21.1

Rincon et al (2005) concluded that methanol, ethanol, and propanol do not seem to be completely miscible in the base oil and as a result they show high POL despite their capabilities in extracting the additive and contaminates (good PSR performance). The experimental results also showed that as the number of carbon atoms in the solvent increases, its ability to remove sludge decreases despite the fact that the solvent became more miscible in the oil (Reis and Jeronimo, 1988). In other words, POL as well as PSR decreases as the number of carbons atoms increases (Reis and Jeronimo, 1988). The experimental study suggests that butanol is a highly effective single solvent in the used oil extraction process and that it outperforms different solvents (lcohols and ketones) with carbon atoms ranging between 1 and 5. Considering the information summarized in Table 4.2 in addition to the previous experimental assessments of several solvents, we recommend that solvents with solubility parameter between 21.5 and 23.5 $(J/m^3)^{1/2}$ should be considered as candidates for the re-refining of used oils. Solvent(s) with solubility parameter less than 21.5 $(J/m^3)^{1/2}$ are highly miscible in both the additives and the base oil, and as a result, will make it very difficult for flocculation of contaminants and additives (upon the addition of a demulsifier such as KOH) and the formation of the sludge phase. On the other hand, any solvent(s), with a solubility parameter higher than 23.5 $(J/m^3)^{1/2}$ will be relatively immiscible in the base oil; which is an undesirable criterion for the solvent as it leads to losses in the base oil.

b. **Vapor Pressure:**

Setting the vapor-pressure bounds is important for the separation process of the solvent-recovery unit. Therefore, a set of simulation tests using the software ASPEN Plus was used to determine these bounds. Based on the simulation results, it was found that any solvent with a vapor pressure between 5 and 150 torr should be included in the consideration set. When the vapor pressure is lower than 5 torr, the separation process becomes very expensive due to the high temperature requirement. High temperature operation does not only come with high utility cost, but it will also decrease the quality of the produced re-refined base oil. Any solvent with vapor pressure higher than 150 torr is considered too volatile, which is not desirable in this extraction process since it reduces the liquid-liquid molecule interaction between solvent and used oil.

c. Viscosity:

Setting the viscosity bounds is crucial for the extraction unit. Therefore, the upper bound was extracted from published experimental data (Reis and Jernimo, 1988). Any solvent with a viscosity between 0.5 and 3.5 cp is included in the consideration of potential solvents. A viscosity higher than 3.5 cp causes the solution to become too viscous, which results in an increase in mass transfer resistance, and thus causes longer extraction time and higher operating cost (stemming from a pumping system). Solvents with typical viscosity less than 0.5 cp are normally in the gas phase, and as a result they should be eliminated from the consideration set.

The ternary cluster representation of the aforementioned constraints is shown in Figure 4.5 where the feasible region is plotted.

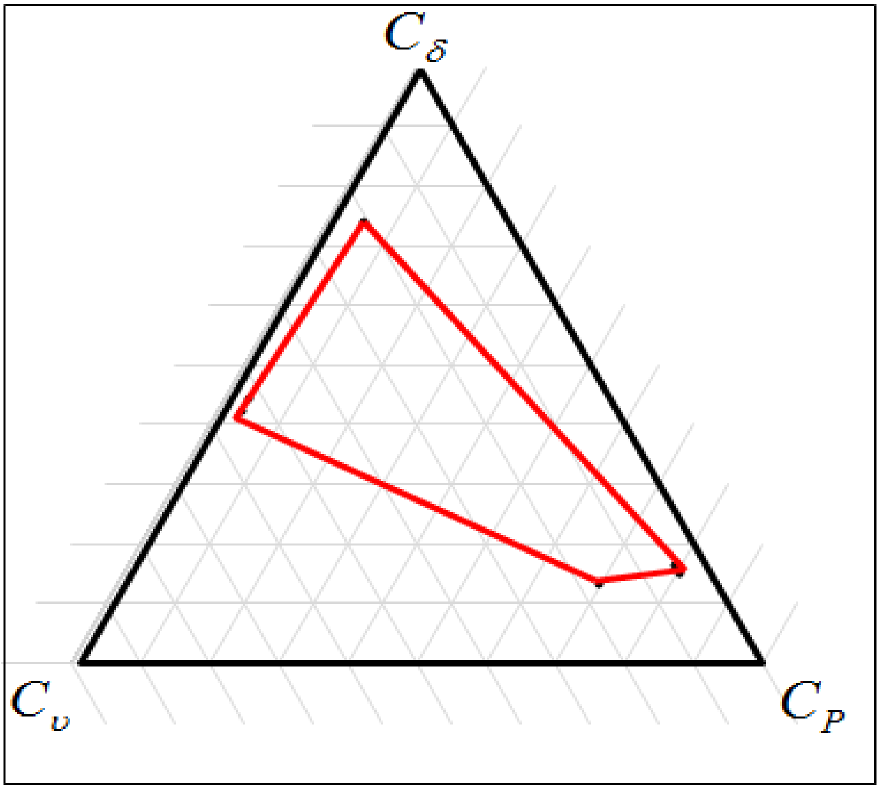

Figure 4.5: The ternary-cluster representation of the feasibility region for the three properties for solvents and blends to be employed in re-refining of used lubricating oil.

As noted before, any solvent or blend of solvents that exists outside the feasible region is eliminated. Solvent blends are constructed to lie within the feasibility region and the lever-arm principle is used to calculate the relative proportions of the mixed solvents. The solvents listed in Table 4.3 are used along with their blends in the case studies. Table 4.3 provides key data that were observed experimentally.

Table 4.3: Experimentally reported performance of number of solvent(s) used in re-refining used oils.

Solvent	Observed Performance	Reference
Hexane	PSR = 0.0	Kamal and Khan (2009)
Butanol	PSR = 4.9	Reis and Jernimo (1988)
Pentanol	PSR = 3.6	Reis and Jernimo (1988)
Propanol+Hexane	PSR = 6.0	Reis and Jernimo (1990)
Methanol	Immiscible with base oil	Reis and Jernimo (1988)
Ethanol	Immiscible with base oil	Reis and Jernimo (1988)
Propanol	Immiscible with base oil	Reis and Jernimo (1988)

Case Study 1: Single Solvents with Experimental Verification

Figure 4.6 shows the cluster representation of the single solvents being studied for lube oil reclamation. Starting with the elimination process, methanol, hexane, and pentanol are located outside the feasible region, and are therefore automatically eliminated from further consideration as single solvents. Although ethanol and propanol fall within the feasible region, their values of the augmented property (AUP) are outside the feasible range for the AUP corresponding to feasible region for the three properties (viscosity, solubility parameter, and vapor presure). Therefore, they have been eliminated as single solvents as well. Finally, butanol lies within the feasible region and passes the AUP feasibility test; making it a viable candidate based on the theoretical property-based calculations.

The theoretical results were compared to experimental data. As indicated by Reis and Jeronimo (1988), it was found that buatnol was the most efficient solvent for this process at a solvent to oil ratio of 3: 1 and extraction temperature of 20 °C. Therefore, the selection of butanol based on the property-integration theoretical procedure is consistent with the experimental observation.

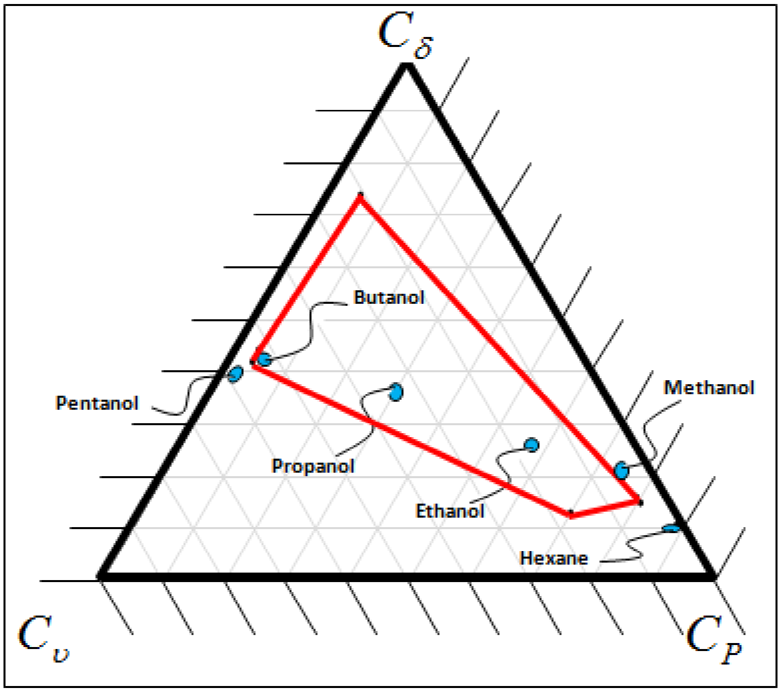

Figure 4.6: Single-solvent representation in the ternary diagram and their positions relative to the feasible region.

Case Study 2: Exclusion of All Possible Infeasible Blends of Two Solvents

Suppose that we are interested in mixing hexane and methanol to get a feasible blend. As can be seen from Figure 4.7, all blends of the two solvents lie on the straight line connecting the two solvents. This straight line lies outside the feasibility region. Therefore, all methanol/hexane mixtures should be eliminated from further consideration as being infeasible. This finding reduces the design effort significantly by eliminating all blends that will not be feasible.

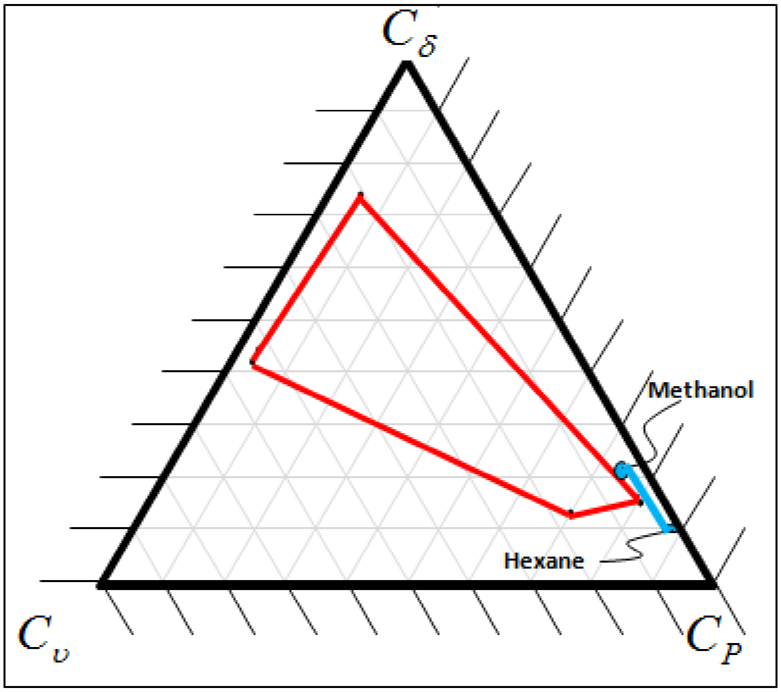

Figure 4.7: Representation of methanol/hexane mixture on the ternary diagram.

Case Study 3: Identifying Ranges of Feasible Blends

As indicated earlier, the elimination of single solvents lying outside the feasibility region does not prevent the possibility of involving these solvents in feasible blends. In this regard, the ternary cluster diagram offers an effective and convenient approach to visually determine feasible blends and the proportions of the participating solvents. For instance, as shown in Figure 4.8, any blend of propanol and hexane is represented by the dashed line connecting the two solvents (shown on the figure as a dashed line). The segment lying outside the feasibility region is labeled as **A**, while the segment lying inside the feasibility region is labeled as **B**. Based on the lever-arm rule, section **A** corresponds to the mixture of hexane to propane ratio greater than 0.9. These are infeasible mixtures. For section **B,** we conducted an AUP test to identify the ratios between the two solvents and validate this performance with the experimentally reported data. After running the AUP test on the mixture, a feasible mixture was found to exist of all mixtures with propanol percentage between 72 and 90%. Reis and Jeronimo (1989) experimentally measured the performance of a mixed solvent of 75% propanol and 25% hexane and concluded that it was an effective blend. This is consistent with the range of feasible solvents identified by our approach.

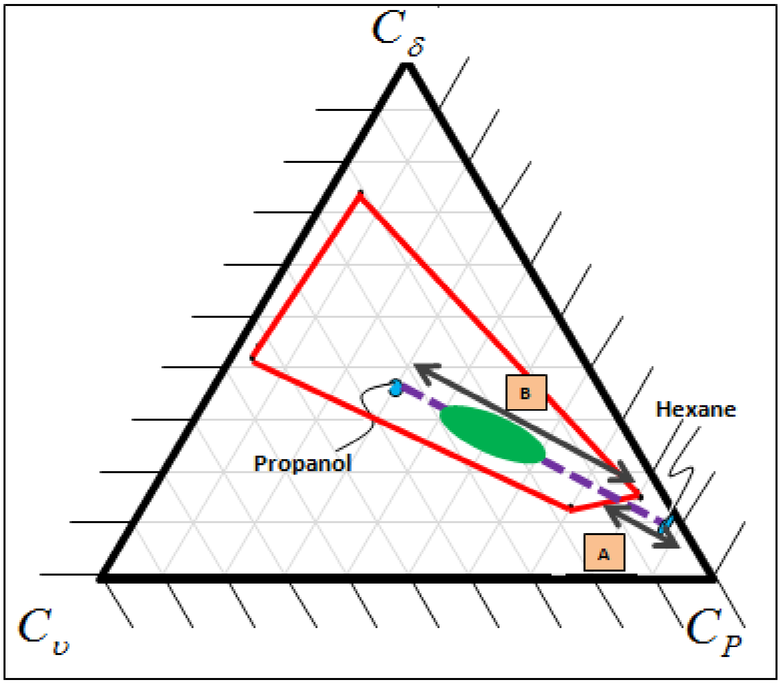

Figure 4.8: Propanol-hexane mixture representation of Case Study 3 on the ternary diagram

4.4 Conclusions

A systematic approach has been developed for the selection of feasible ranges of solvents and solvent blends for lube-oil reclamation. A property-integration framework was adopted as the basis for design. Specifically, property clusters were used to graphically represent the process and candidate solvents. Three principal properties were used: solubility parameters, pressure, and viscosity. A combination of reverse-simulation and experimental results was used to set the boundaries on the constraints required by the process. The feasibility of single solvents and solvent blends was identified through the ternary-cluster visualization diagram. Infeasible solvents and solvent blends were determined and removed from further consideration. Also, all ratios of solvent blends leading to feasible mixtures were determined. Three case studies were solved and compared to demonstrate the effectiveness of the devised approach. Experimental observations were used to confirm the validity of the approach and theoretical results.

In addition to its effectiveness in selecting solvents and blends and designing lube-oil reclamation processes, the proposed approach also serves as the basis for guiding experimental work by identifying feasible and promising solvents and blends and by shedding light on the insights on the design aspects.

Recommended future work includes the development of an optimization approach to extend the applicability of the procedure to more than three key properties and to automate the decision-making process and use it as a basis for the optimization of solvent selection and process design.

5 A SYSTEMATIC TECHNO-ECONOMICAL ANALYSIS FOR THE SUPERCRITICAL SOLVENT FISCHER TROPSCH SYNTHESIS

5.1 Introduction

Annually, 2.7 billion gallons of lube oil are sold in the United States. About 2.7 billion gallons is consumed, and the rest is considered used oil. 500 million gallons are left without any recycling program (Project Rose, 1990). The mishandling of used lubricating oil poses a major environmental crisis. It has been mainly dumped in land field, burned as fuel, etc (Figure 5.1).

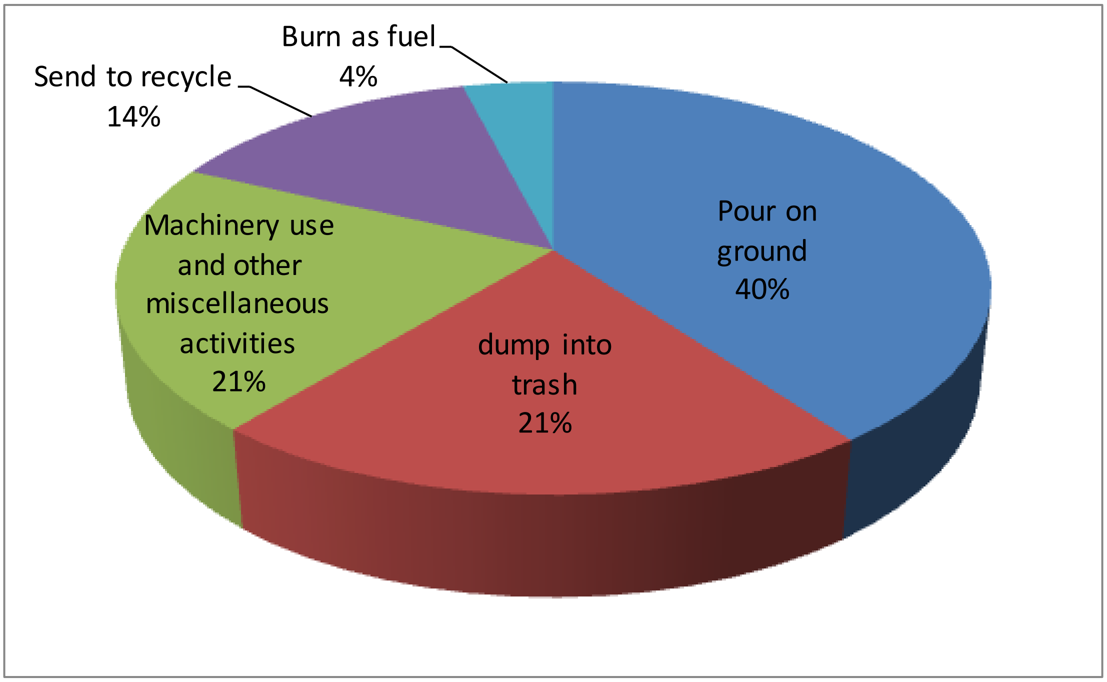

Figure 5.1: Common Used oil disposal methods (Project Rose 1990)

Most of these actions are harmful for the environment such as leakage into waterways, and irresponsible toward our future generation duties such as depletion of natural resources. The recycling of used lubricating oil is a more sustainable form of action. It makes sense not only from the environmental point of view but economic as well. If the used oil is fed to a boiler, a net saving of $0.65/gal could be achieved. However, a net saving of $1.50/gal could be realized if it is recycled (Project Rose, 1990). Chemical and physical methods have been developed to recycle the used lubricating oil. The chemical method is acid-sludge re-refining technique. It involves the use of sulfuric acid as a solvent. The main disadvantage of such a process is the acidic sludge produced. It is more harmful than the base oil itself. The other re-refining technique is the physical method where the separation occurs at very high temperature which causes the lube oil to break down. Therefore, the main disadvantages of this technique are the low quality base oil produced, and high volume requirement for economic purposes. Solvent extraction yields the advantages and eliminates the disadvantages of both processes. High volume is not required; organic sludge is produced; high quality base oil is produced.

The recycling of used lubricating oil not only helps in the preservation of natural resources, but also reduces the dependency on foreign oil. This work is unique because the developed optimization formulation not only reveals the identity of the optimal solvent but also targets the optimal operating conditions based on profitability.

5.2 Solvent Extraction Process Description and Problem Statement

Due to the stability of the heavy base oil molecules, the base oil itself stays intact after usage. One gallon of lube oil yields 0.7 gallon of re-refined oil (Everest, 2005). The re-refining of used lubricating oil's job is to completely remove the metals and worn additives from base oil. This is not an easy task to accomplish. The solvent extraction process could be designed in many different ways. However, there are three essentials unites needed in order to accomplish the desired task. If further detailed design of units is requested, simulation data will be needed in order to include all design elements in the process. Therefore, a generic block flow diagram of the solvent extraction process could be shown in Figure 5.2.

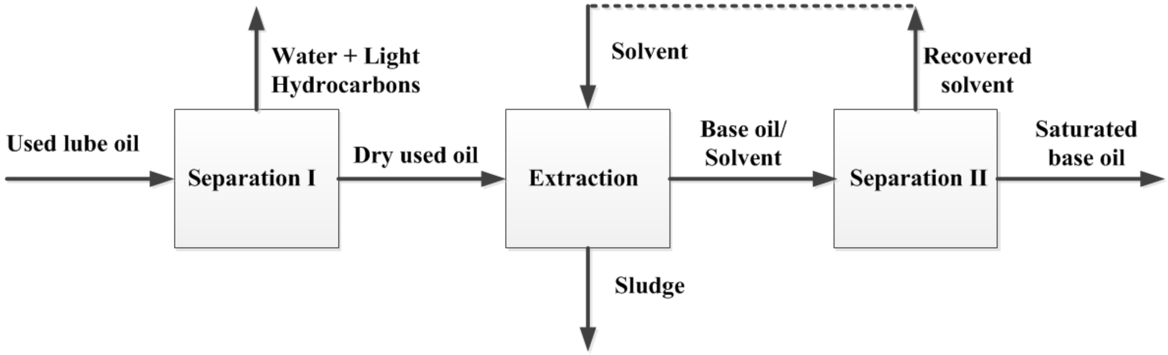

Figure 5.2: Simplified block flow diagram for the solvent extraction process of recycling used lubricating oil.

Used lubricating oil is fed to separation unit I (atmospheric distillation column) to remove water and light hydrocarbons. Dry used oil is collected as bottom of the column. Then, it is mixed with the organic solvent. Two phase solution is formed. Organic sludge (bottom phase) is constituted of contaminants and lost oil/solvent mixture. The upper phase contains the base oil and solvent mixture. The organic sludge is easy to handle. For instance, it could be collected and sold for ink or asphalt industries. The oil/solvent mixture is sent to separation unit II for complete regeneration of solvent. In order to prevent the breakdown of base oil molecules at high temperature, it is suggested to use both atmospheric and vacuum distillation columns.

5.3 Problem Statement

This section presents the model formulation for the optimization process, and these equations are based on the representation of figure 5.3.

Note that figure 5.3 includes different equipments/units which may or may not be used to accomplish the desired task. Therefore, it has been left to the optimization to decide whether certain equipments are needed or not. Also, figure 5.3 shows only three units, but the formulation includes the option of infinite number of stages. The optimization will decide if it is worth to spend the extra capital investment for the extra unit(s) to be purchased in order to remove the excess contaminants.

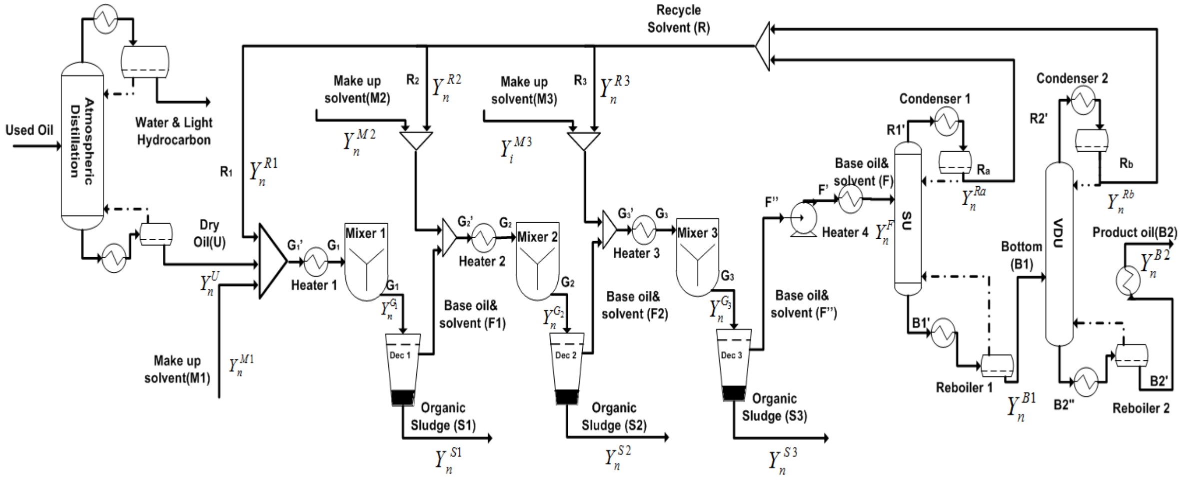

Figure 5.3: Process Flow Diagram for the solvent extraction process of recycling used lubricating oil.

There are many rooms for optimization within the process. The extraction unit depends on three major factors. First of all, the solvent type and cost are very important variables to be considered in the formulation. Solvent type affects the percent sludge removal (PSR) and Percent oil Loss (POL). Note that PSR and POL are primary parameters used for the evaluation of extraction performance. It is desired to yield the lowest POL and the highest PSR possible. Another major factor is the operating temperature. For instance, the higher the temperature the higher the miscibility of solvents in oil is, but the lower the PSR is. Therefore, there is an optimal temperature at which the chosen solvent should operate taking into account cost of heating simultaneously. Last but not least, solvent to oil ratio (SOR) poses limitation on both POL and PSR. In order to achieve solvent saturated mixture, high SOR is desired. However, the higher the SOR is, the more make-up solvent and regeneration cost are associated with such a desire. Also, it is very important to note as it has been shown experimentally that there is an optimal SOR at which the addition of more solvent does not cause further separation. In other words, at $SOR > SOR_{optimal}$, POL and PSR remain almost constant. This will be shown later in the case study. It is worth to note that the limitation on the PSR affects the number of stages required in order to remove all contaminants. This, in terms, affects the capital and operating cost of the extraction unit.

Next, the separation unit is part of the process, it has been considered in the holistic optimization formulation. The optimal separation temperature in both the atmospheric (SU) and vacuum distillation (VDU) has been targeted. Temperature as well as solvent type and SOR affect the solvent recovery and operating and capital cost of both columns including condensers and reboilers. Therefore, the consideration of both units simultaneously is essential and shows the uniqueness of this work.

5.3.1 Mass Balance

This section presents the material balances in the representation of Figure 5.3.

First, the material balance around Mixer 1 is stated as follows.

$$M_1 + U + R_1 = G_1 \tag{1}$$

In previous equation M_1 is solvent make up fed to mixer 1, U is the mass flowrate of dry based oil, R_1 is the flowrate of regenerated/recycled solvent to extraction stage 1, G_1 is the flowrate of mixture fed to stage 1.

Material balance around mixer i with i> 1 can be stated as follows:

$$G_i = M_i + F_{i-1} + R_i \qquad \forall\, i > 1 \tag{2}$$

where M_i is the flowrate of solvent make-up fed to mixer i, F_{i-1} is the flowrate leaving the top of decanter $i-1$ before fed to the next mixer i, R_i is the flowrate of recycled/recovered solvent to stage i, and G_i is the flowrate of mixture fed to decanter i.

The material balance around decanter i is:

$$G_i = F_i + S_i \qquad \forall i \in I \tag{3}$$

with i is the number of stages and it takes values of 1,2,3…istages, F_i is the flowrate of solvent/oil mixture leaving decanter i, and S_i is the flowrate of sludge leaving decanter i.

Material balance around atmospheric column (SU):

$$R_a + B_1 = F \tag{4}$$

where R_a is the flowrate of the recovered solvent leaving the top of the atmospheric column, B_1 is the bottom of the atmospheric column, F is the flowrate leaving the top of the last decanter.

Material balance around vacuum distillation column (VDU):

$$B_1 = R_b + B_2 \tag{5}$$

where R_b is the flowrate of the recovered solvent leaving the top of the vacuum column, B_2 is the bottom of the vacuum column which should include the saturated base oil.

Material balance of recovered solvent:

$$R = \sum_{i=1} R_i = R_a + R_b \qquad \forall i \in I \tag{6}$$

5.3.2 Component Material Balance

Similar to the mass balance, there are component balances for the base oil, contaminants and solvent in the different sections of the diagram.

The component balance around mixer 1 is stated as follows:

$$M_1 * Y_n^{M1} + U * Y_n^{U} + R_a * Y_n^{R_a} = G_1 * Y_n^{G1} \qquad \forall\, n \in N \tag{7}$$

In previous equation Y_n is the composition by weight of component N given, where $N = \{1,2,3\}$, and n=1 corresponds to the base oil, n=2 is used for the contaminants and n=3 is for the solvent.

Component balance around mixer i and decanter i consecutively:

$$M_i * Y_n^{Mi} + F_{i-1} * Y_n^{F_{i-1}} + R_i * Y_n^{Ri} = G_i * Y_n^{Gi} \qquad \forall\, n \in N \tag{8}$$

$$G_i * Y_n^{Gi} = F_i * Y_n^{Fi} + S_i * Y_n^{Si} \qquad \forall\, n \in N \tag{9}$$

Component balance around SU and VDU consecutively:

$$R_a * Y_n^{Ra} + B_1 * Y_n^{B1} = F * Y_n^{F1} \qquad \forall\, n \in N \tag{10}$$

$$R_b * Y_n^{Rb} + B_2 * Y_n^{B2} = B_1 * Y_n^{B1} \qquad \forall\, n \in N \tag{11}$$

Component balance for the total recycled solvent is as follow:

$$R * Y_n^{R} = R_1 * Y_n^{R1} + R_2 * Y_n^{R2} \qquad \forall\, n \in N \tag{12}$$

5.3.3 Heat Balance

The heat balance around heat exchanger *i* corresponding to stage *i* in the extraction unit is expressed as follow:

$$Q_{Heater\_i} = G_i * C_p^{mix\_i} * (T^{Gi} - T^{Gi'}) \tag{13}$$

where Q_{heater_i} is the heat load needed to increase/decrease the temperature from its value T_{Gi}' to an optimal extraction temperature T_{Gi}, and $C_P^{mix\_i}$ is the heat capacity of the mixture.

Since the extraction will occur in liquid phase, it can be correlated to the pure component values as follow:

$$C_p^{mix\_i} = \sum_n Y_n^{Gi} * C_{p_n} \tag{14}$$

where C_{pn} is the heat capacity of pure component n and it is function of temperature.

The heat balance data around both reboilers and condensers of the distillation columns could be extracted from ASPEN PLUS and to determine the dependence of operating temperature.

5.3.4 Equilibrium Equations

The percent sludge removal (PSR) is the mass of dry sludge being removed in grams per 100 g of used oil (Reis and Jernimo, 1988).. Therefore, the PSR from stage 1 is expressed as follow:

$$PSR_i = \frac{Y_2^{Si} * S_i}{(1 - Y_3^{Gi}) * G_i} \qquad \forall i \in I \qquad (15)$$

$$PSR_i = PSR(solvent\,type, T_i, SOR_i) \qquad (16)$$

The percent oil loss is defined as the mass of base oil lost with the sludge in grams per 100 g of used oil (Reis and Jernimo, 1988, and Elbashir et al., 2002), and it is shown in the following equation:

$$POL_i = \frac{Y_1^{Si} * S_i}{(1 - Y_3^{Gi}) * G_i} \qquad \forall i \in I \qquad (17)$$

$$POL_i = POL(solvent\,type, T_i, SOR_i) \qquad (18)$$

A new variable *K* is defined to express the equilibrium equations in both the SU and VDU units. K_n is the ratio of the mass fraction of component *n* of the bottom of the column divided by the mass fraction of top stream. Therefore, the K relationship for the component *n* in both SU and VDU is expressed consecutively as follow:

$$K_n^1 = \frac{Y_n^{B1}}{Y_n^{Ra}} \qquad \forall n \in N \qquad (19)$$

$$K_n^2 = \frac{Y_n^{B2}}{Y_n^{Rb}} \qquad \forall n \in N \qquad (20)$$

$$K_n = K\left(T^{separation}, P^{Separation}\right) \qquad (21)$$

5.4 Optimization Formulation

Most of the work done on the solvent extraction optimization is to find the optimal solvent with the lowest POL and highest PSR regardless of cost. This might be a good indication for an optimal solution, but it is not sufficient from a holistic approach. A look at the process as a whole is necessary to find the optimal solution. As is the case in most optimization formulations, an objective function that maximizes profit is needed, and for this case the net profit is stated as follows:

$$Maximize\ \mathrm{Pr}ofit = Sales - Cost \tag{22}$$

$$Sales = Sale\_oil + Sale\_sludge \tag{23}$$

$$Sale\_oil = \left(B_2 * oil\_\cos t + S * Sludge\_\cos t\right) * w \tag{24}$$

where *W* is the hours of operation per year, *Oil_cost* is the cost of base oil per Kg, *Sludge_cost* is the cost of sludge per Kg that could be obtained from ink or asphalt industries.

Note that *S* is the combination of all the sludge leaving the extraction unit and could be expressed as follows:

$$S = \sum_i S_i, \qquad \forall i \in I \tag{25}$$

Then, the annual cost is the summation of both annual operation cost and annual capital cost, and it could be calculated as follow:

$$Cost = Cost\_Capital + Cost\_Operation \tag{26}$$

The capital cost includes all major pieces of equipment in the whole process and it is defined as:

$$Cost\_Capital = \sum_i Cost\_Hex_i + \sum_i Cost\_Decanter_i + \sum_i Mixer_i + Cost\_SU + Cost\_VDU \qquad (27)$$

where *Cost_Hex*$_i$ is the annual cost of the heat exchanger needed in stage *i,* which is responsible on bringing the temperature of mixture to optimal extraction temperature, *Cost_Decanter*$_i$ and *Cost_Mixer*$_i$ are the annual costs for the decanter and the mixer in stage *i*, respectively. *Cost_SU* is the annual cost of the atmospheric column needed for the separation, this includes the capital cost of the condenser and reboiler associated with the column, and *Cost_VDU* is the annual capital cost of the vacuum distillation column required, this includes the capital cost of condenser and reboiler associated with the column.

The equations that describe the annual capital cost of these equipments are shown below:

$$Cost\_Heater_i = C_{FC}^{Heater\,i} + C_{vc}^{Heater\,i} * (A^{Heater\,i})^{\alpha\, i} \qquad (28)$$

$$Cost\_Mixer_i = C_{FC}^{mixer\,i} + C_{vc}^{mixer\,i} * (V^{mixer\,i})^{\alpha\, i} \qquad (29)$$

$$Cost\_Decanter_i = C_{FC}^{Decanter\,i} + C_{vc}^{Decanter\,i} * (A^{Decanter\,i})^{\alpha\, i} \quad (30)$$

$$Cost\_SU = f(F, T^F, P^F, Y_n^F, Y_n^{Ra}, Y_n^{B1}) \qquad (31)$$

$$Cost\_VDU = f(B1, T^{B1}, Y_n^{B1}, Y_n^{Rb}, Y_n^{B2}) \qquad (32)$$

Another major cost that contributes to the total annual cost is the annual operation cost, which depends on so many factors. It includes the cost of heating/cooling needed for an optimal operating condition as well as the solvent make up cost. It is calculated as follows:

$$Cost\_Operation = \sum_i Cost\_Heating_i + \sum Cost\_Condensing + \sum Cost\_Reboiling + Make\_up\_Cost \quad (33)$$

Note that *Cost_Heating$_i$* is the annual heat duty cost of stage *i* required to increase the mixture temperature T_i to the optimal extraction temperature T_i^{opt}. This cost is obtained as the product of heat duty Q_i times the heating utility cost multiplied by the yearly hours of operation:

$$Cost\_Heating_i = Q_i * Cost\_HU * w \quad (34)$$

where *Cost_Condensing* is the total condensing cost required by both columns and *Cost_Reboiling* is the total reboiling cost required by both columns.

The *Make_up_cost* is expressed as follow:

$$Make\_up\_cost = \sum_i M_i * Cost\_Solvent * w \quad (35)$$

5.5 Case Study and Results

This section presents a case study to show the applicability of the proposed optimization formulation.

5.5.1 Data Collection

To illustrate the applicability of the proposed optimization approach, a case is presented. In this case, Methyl Ethyl Ketone (MEK) and Butanol have been chosen as solvents of interest. As it has been proven previously (Nimir, 1997), MEK yields the lowest POL, and Butanol performs best at PSR. It is good to put these values in terms of economics, and let the optimization decides the overall optimal solvent. Experimental results have been used to collect PSR and POL data (Katiyar, 2010). These results are presented in figures 5.4 and 5.5. All other data have been extracted from Aspen Plus simulation.

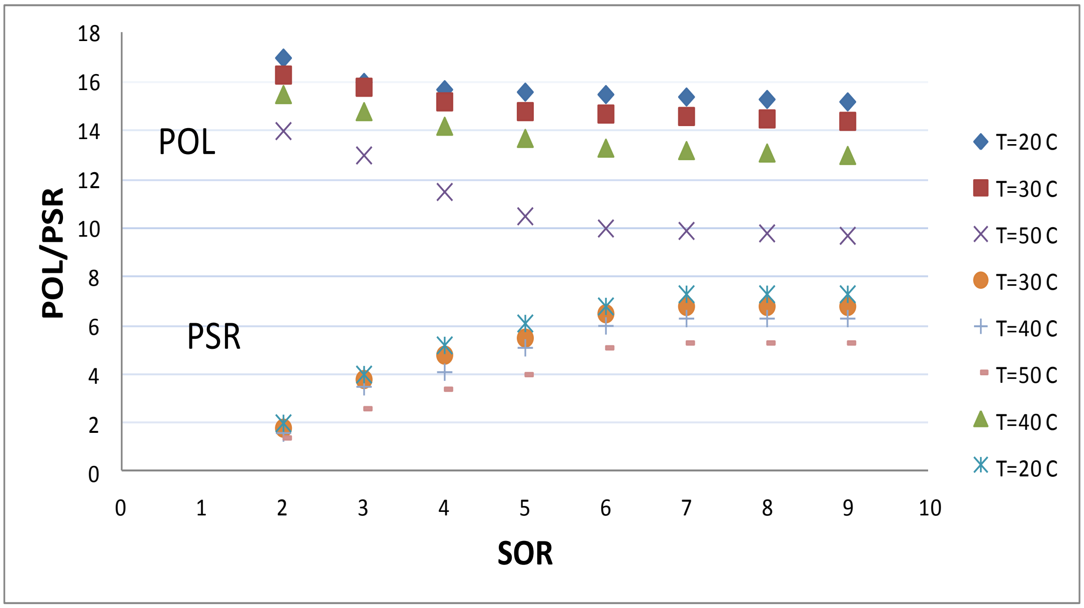

Figure 5.4: Effect of solvent to oil ratio (SOR) and Temperature (T) on percent oil loss and percent sludge removal (POL/PSR) using 1- Butanol as a solvent (Katiyar 2010).

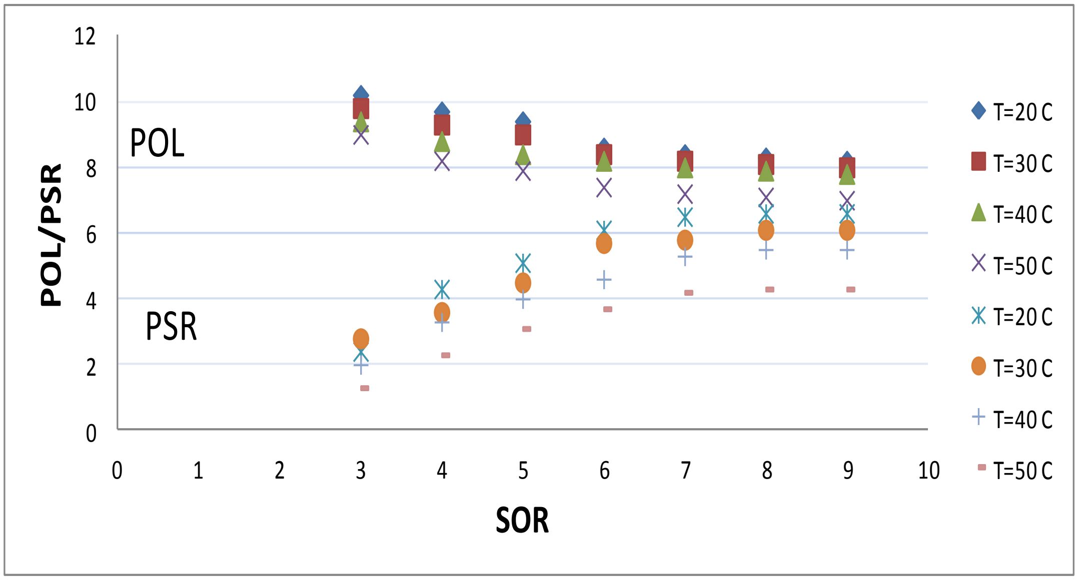

Figure 5.5: Effect of solvent to oil ratio (SOR) and Temperature (T) on percent oil loss and percent sludge removal (POL/PSR) using MEK as a solvent (Katiyar, 2010).

Figures 5.4 and 5.5 show that the increase in temperature leads to decrease in the *POL*. This is an indication of increase of base oil miscibility in the solvent as the temperature increases. However, from the experimental results, it can be noticed that there is a trade off since the increase in temperature decreases the PSR as well. This makes it an interesting optimization problem. It is desirable to achieve an optimal extraction temperature that yields the highest *PSR* and lowest *POL* possible based on profitability. In addition, Figures 5.4 and 5.5 show that the increase in *SOR* increases the *PSR* and decreases the *POL*. However, the increase in *SOR* reaches a critical value after which the addition of solvent does not change the *POL* and *PSR*. Note that the more solvent is used the bigger the equipment (higher capital cost) will be needed the more solvent make-up will be purchased, and the more operating solvent recovery cost will be indicated. Note that deriving equations (16) and (18) from both figures is not an easy task to perform. Lingo optimization software has been used to derive these equations. This was done by composing an objective function that minimizes the error between the experimental and calculated values. A generic equation with multiple unknown parameters and two variables (*SOR* and *T*) was assigned in order to evaluate the calculated values. The value of the error squared was less than 4 in all cases given 32 data points for each equation. This indicated good plot fitting approach, and shows that the generic equation provided was relatively good.

$$POL_i^{BUTANOL} = 15.691 + 6.51903\exp(-0.41338\,\mathrm{SOR}_i) - 0.15175 \times \mathrm{T}_i + 2.51851 \qquad (35)$$

$$POL_i^{MEK} = 6.71806 + 6.89802\exp(-0.386576\,\mathrm{SOR}_i) - 0.042875 \times \mathrm{T}_i + 2.313249 \qquad (36)$$

$$PSR_i^{BUTANOL} = 3.291565 \times \ln(1.669866\,\mathrm{SOR}_i) - 0.0555 \times \mathrm{T}_i \qquad (37)$$

$$PSR_i^{MEK} = 3.303513 \times \ln(1.331624\,\mathrm{SOR}_i) - 0.062 \times \mathrm{T}_i \qquad (38)$$

Note that T_i is in degree Celsius.

To highlight the importance of operation cost, it is assumed that the process already exists, and no need to purchase any pieces of equipment. Therefore, the capital cost is ignored from the objective function. The distillation columns separation data have been obtained using Aspen Plus (refer to Appendix A). Note that condensing, reboiling, and extraction heat duties were extracted from Aspen Plus as well.

Finally, binary variables *Z₁* and *Z₂* were assigned for Butanol and MEK consecutively, and the Big-M formulation was used to relax most constraints. This could be illustrated in the following set of equations:

$$\mathrm{P}OL_i \leq \mathrm{P}OL_i^{BUTANOL} + 100 \times (1 - \mathrm{Z}_1) \tag{39}$$

$$\mathrm{P}OL_i \geq \mathrm{P}OL_i^{BUTANOL} - 100 \times (1 - \mathrm{Z}_1) \tag{40}$$

$$\mathrm{P}OL_i \leq \mathrm{P}OL_i^{MEK} + 100 \times (1 - \mathrm{Z}_2) \tag{41}$$

$$\mathrm{P}OL_i \geq \mathrm{P}OL_i^{MEK} - 100 \times (1 - \mathrm{Z}_2) \tag{42}$$

$$Z_1 + Z_2 = 1 \tag{43}$$

5.5.2 Results and Discussions

The base case assumes that three extraction stages exist with a capacity of *SOR* less than or equal to 5:1. Also, the used oil composition is 85% base oil and 15% contaminants. Solvents and base lube oil costs were extracted from ICIS pricing website and they are summarized in Table 5.1 (ICIS website):

Table 5.1: Solvents and oil costs

	Cost $/kg
Base oil	1.75
Butanol	1.54
MEK	0.75

It is assumed that the organic sludge could be sold for $0.5/kg less than three times the value of base oil. It is also assumed that the three extraction units are responsible on removing a total of more than 80% of the contaminants. Another major constraint is that base oil should not be exposed to temperature higher than 140 °C in order to eliminate the risk of breaking it down and reducing its value. No data was available for the percent of solvent loss with the contaminant. Therefore, results were generated at 5 % and 10% of solvent loss. The optimization chooses MEK as the optimal solvent in both cases. This is due to lower MEK cost and its higher ability to conserve the base oil (lower POL). At 5 and 10% solvent loss, the optimal extraction temperature in all three stages was 20 °C. SOR values are summarized in Table 5.2.

Table 5.2: SOR values at 5% and 10% solvent losses.

Solvent loss	SOR1	SOR2	SOR3
5%	4	4.5	4.9
10%	4.3	4.5	4.7

The values are not too different. The reason lies behind the major constraint of 20% of contaminants removal. In order to study the effect of that constraint on the optimal operating extraction condition as well as the solvent selection, a series of Lingo models were ran at 5% and 10% solvent loss, and the results are tabulated in tables 5.3 and 5.4.

Table 5.3: Solvent selection and extraction operating conditions at different total % sludge removed taking into account 5% of solvent is lost at each stage.

	5% of Solvent Loss						
Total % Sludge removed	T1 ©	T2 ©	T3 ©	SOR1	SOR2	SOR3	Solvent
33.3	20	50	50	3.3	3.67	3.9	MEK
46.7	20	50	50	3.3	3.67	3.9	MEK
53.3	20	50	50	3.3	4	4	MEK
60.0	20	30	50	3.5	3.9	4.3	MEK
66.7	20	20	50	3.7	4.1	4.6	MEK
73.3	20	20	32	3.8	4.2	4.7	MEK
80.0	20	20	20	4	4.5	4.9	MEK
83.3	20	20	20	3.3	4	5	Butanol

Table 5.4: Solvent selection and extraction operating conditions at different total % sludge removed taking into account 10% of solvent is lost at each stage

Total % sludge removed	10% Solvent Loss						
33.3	T1 ©	T2 ©	T3 ©	SOR1	SOR2	S0R3	Solvent
46.7	20	20	50	2.2	2.3	2.4	MEK
66.7	20	20	26	2.4	2.6	2.7	MEK
73.3	20	20	20	3.3	3.5	3.7	MEK
80.0	20	20	20	4.2	4.5	4.7	MEK
83.3	20	20	20	3.3	4	5	Butanol

As the total percent sludge removed increases, the temperature decreases and the *SOR* increases. MEK is the optimal solvent in all cases except at total %sludge removed higher than 83.3%. This is due to the physical ability limitation of MEK to remove the contaminants at higher level. Because Butanol is better sludge removal solvent, it was selected at total % sludge higher than 83.3. Note that this conclusion holds true in both cases of 5% and 10% solvent loss. These results would have been different if the SOR<5 constraint was ignored. At lower total % sludge removed, it is worth to note that T2 and T3 values at 5% solvent loss are higher than T2 and T3 values at 10% solvent loss. However, this is accompanied by higher *SOR2* and *SOR3* values in the 5% than the 10% solvent loss. The reason is the optimization preference in the 5% solvent loss to increase the temperature indicating lower oil loss and sacrificing higher *SOR* (higher solvent loss) at 5% rate of solvent loss. However, in the 10% solvent loss, the optimization tendency was to decrease the temperature indicating higher percent oil loss and decreasing *SOR* to decrease the amount of solvent loss at 10% rate of solvent loss.

Another important factor to be studied is the MEK and Butanol prices variation. If MEK price stays the same at \$0.75/kg, at what price Butanol or a solvent that performs the same as Butanol should be in order to be optimal? This solvent price value is different in both 5% and 10% solvent loss cases. In the 5% solvent loss case, Butanol or equivalent solvent should be at \$0.35/kg or lower to become favored. In the 10% solvent loss case, Butanol or equivalent solvent should be at \$0.55/kg or lower in order to become favored over MEK.

Now, if Butanol price stays the same at \$1.54/kg, up to what price MEK or a solvent that performs the same as MEK stays favored over Butanol? This value is different in both 5% and 10% solvent loss cases. In the 5% solvent loss case, MEK or equivalent solvent could be at a cost of \$1.7/kg or lower to stay favored over butanol. In the 10% solvent loss case, MEK or equivalent solvent could be at \$1.54/kg or lower in order to stay favored over Butanol.

Another sensitivity analysis is done over the quality of base oil. It is assumed that the *SOR* constraint is not valid, and therefore *SOR* could have a value greater than 5. This was done by the keeping the constraint on the contaminant composition leaving the last extraction unit with base oil/solvent mixture to be less than 3% of the used oil fed to the first extraction unit. The quality of base oil was varied by changing the composition of base oil in the feed from 85% to 90% and 80%. The results are summarized in Tables 5.5 and 5.6:

Table 5.5: Result summary of the effect of base oil quality taking into account 5% solvent loss in each stage.

	5% Solvent Loss						
% Base oil in the feed	T1	SOR1	T2	SOR2	T3	SOR3	Solvent
90%	20	3.3	50	3.7	50	3.9	MEK
85%	20	4	20	4.5	20	4.9	MEK
80%	20	7.3	20	8	20	9.1	MEK

Table 5.6: Result summary of the effect of base oil quality taking into account 10% solvent loss in each stage.

	10% Solvent Loss						
% Base oil in the feed	T1	SOR1	T2	SOR2	T3	SOR3	Solvent
90%	20	2.4	20	2.5	20	2.6	MEK
85%	20	4	20	4.5	20	4.9	MEK
80%	20	7.7	20	8.1	20	8.6	MEK

Tables 5.5 and 5.6 show that MEK is the optimal solvent, and this is due to its lower cost and its high ability in preserving the oil (low *POL*). The results in both tables are similar in the 85% and 80% case. However the results are different in the 90% case. This is due to the operating condition flexibility of MEK in removing lower amount of contaminants. In the case of 10% solvent loss, lower temperature and lower *SOR* were favored in order to decrease the amount of solvent loss. In the case of 5% solvent loss, higher temperature and higher *SOR* were favored since the solvent loss is at lower rate. In the 85% and 80%, MEK does not have a lot of operating condition flexibility in removing the large amount of contaminants. The low temperature and high *SOR* were necessary to satisfy the total sludge removal constraint.

Note that these results depend heavily on the assumptions made as well as the solvents chosen for this case study. The results will be a lot different if they were to change. Also, it would be different if this case study gave the optimization the flexibility of deciding the number of units based on cost as shown in the generic formulation. Also, note that this formulation could be applied not only to single solvents as shown in the case study, but it also applies to solvent blends as well.

5.6 **Conclusions**

This paper presents an optimization formulation for the optimal production oil from used oil through different solvents and configurations. This formulation takes into account the capital cost as well as the operating cost associated with each solvent. The proposed model was tested for the use of Butanol and MEK as solvent considering experimental data and data obtained from simulation. Results show that Butanol performs better from PSR point of view; whereas, MEK performs better from POL stand point. In most cases, MEK was favored due to its lower cost and higher ability to preserve our valuable base oil product.

As of future work, it would important to include safety metrics in the formulation in order to eliminate the risk of using hazardous solvents as well as the decrease the risk associated to the operating conditions required. In addition, it will be important to address a case study with the inclusion of the capital cost and show its effect on the optimal results. Finally, heat integration could be another economic incentive.

6 CONCLUSIONS AND RECOMMENDATION FOR FUTURE WORK

This work has introduced systematic approaches for the recycle and reclamation of material utilities and spent products. In the area of material-utility (e.g., water) recycle; a new process-synthesis procedure has introduced to addresses, for the first time, the simultaneous handling of concentrations, temperature, and properties to characterize the process streams and constraints. This has been done, taking into account the interdependency of properties and their dependency on concentrations and temperature. An optimization formulation has been developed to identify optimal allocation of sources to sinks that will minimize the network cost while satisfying all process and environmental constraints. A case study on water recycle in a phenol production plant has been solved.

A systematic approach has also been developed for the selection of feasible ranges of solvents and solvent blends for lube-oil reclamation. A property-integration framework was adopted as the basis for design. Specifically, property clusters were used to graphically represent the process and candidate solvents. Three principal properties were used: solubility parameters, pressure, and viscosity. A combination of reverse-simulation and experimental results was used to set the boundaries on the constraints required by the process. The feasibility of single solvents and solvent blends was identified through the ternary-cluster visualization diagram. Infeasible solvents and solvent blends were determined and removed from further consideration. Also, all ratios of solvent blends leading to feasible mixtures were determined. Next, an optimization formulation was developed to identify the key design and operating variables of the system as well as the selection of the optimal solvent(s) for extraction. Key parameters were considered such as percent oil loss (POL), percent sludge removal (PSR), and their dependency on temperature and solvent to oil ratio (SOR). Three case studies were solved and compared to demonstrate the effectiveness of the devised approach. Experimental observations were used to confirm the validity of the approach and theoretical results.

In addition to its effectiveness in selecting solvents and blends and designing lube-oil reclamation processes, the proposed approach also serves as the basis for guiding experimental work by identifying feasible and promising solvents and blends and by shedding light on the insights on the design aspects.

Recommended future work includes the following:

- Inclusion of heat integration in the design of material-utility recycle networks
- Incorporating additional properties (e.g., density) in the reclamation of lube oil
- Comparison of extraction-based reclamation networks to other recovery and disposal alternatives (e.g., thermal conversion)
- Incorporation of safety metrics for the solvents and the process into the optimization formulation to generate inherently safer designs
- Design of flexible systems that can respond to the dynamic fluctuations in the characteristics of wastewater streams.
- Inclusion of life cycle analysis for the used materials and the designed processes.

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APPENDIX A

Water Network Coding

```
Data:
        NSOURCE=3;
        NFRESH=2;
        NSINK=3;
        NWASTE=1;
!       NCOMPOSITION=1;
!       NPROPERTY=1;

Enddata

Sets:
        Source/1..NSOURCE/:SRInx;
        FreshSource/1..NFRESH/:FRInx;
        Sink/1..NSINK/:SKInx;
        Waste/1..NWASTE/:WasteInx;
!       Composition/1..NCOMPOSITION/:CompInx;
!       Property/1..NPROPERTY/:PropInx;
Endsets

Sets:
        flowSRtoSK(Source,Sink):flowSRSK;
        !segregated mass flowrate from process source i to sink j;
        flowSRtoWaste(Source,Waste):flowSRWaste;
        !segregated mass flowrate from process source i to the waste stream;
        TotalflowSource(Source):TotalFlowSR;                                    !total
mass flowrate from process source i;
        flowFreshtoSK(FreshSource,Sink):flowFRSK;
        !segregated mass flowrate from fresh source r to sink j;
        Fresh(FreshSource):flowFR, costFR;                                      !total
flowrate consumed and unit cost of fresh source r;
        flowSink(Sink):inflowSK;
        !total mass flowrate inlet process sink j;
        FlowWaste(Waste):inflowWaste,costWaste;                                 !total
mass flowrate and unit cost of the waste;

        CompositionFresh(FreshSource):compFR,molecompFR,moleWaterFR;
        !composition of process source r;
        TemperatureFresh(FreshSource):tempFR;
        !temperature of process source r;
```

```
        PropertyFresh(FreshSource):propFR;
        !property of fresh source r;
        heatCapacityFresh(FreshSource):CpFR;
        !heat capacity of process source r;

        CompositionSource(Source):compSR,molecompSR,moleWaterSR;!composition
of process source i;
        TemperatureSource(Source):tempSR;
        !temperature of process source i;
        PropertySource(Source):propSR;
        !property of process source i;
        heatCapacitySource(Source):CpSR;                                    !heat
capacity of process source i;

        CompositionSink(Sink):incompSK,mincompSK,maxcompSK, molecompSK,
moleWaterSK, moleSink; !inlet, minmum and maximum composition of process sink j;
        TemperatureSink(Sink):intempSK,mintempSK,maxtempSK;                 !inlet,
minmum and maximum temperature of process sink j;
        PropertySink(Sink):inpropSK,minpropSK,maxpropSK;                    !inlet,
minmum and maximum property of process sink j;
        heatCapacitySink(Sink):CpSK;
        !heat capacity of process sink j;

        deltaEnthalpySink(Sink):deltaH_Sink,A12,A21,Ln_Gamma1,Ln_Gamma2,Gam
ma1,Gamma2;                !enthalpy change in the mixing node before process sink j;
        deltaEnthalpyWaste(Waste):deltaH_Waste,Aw12,Aw21,Ln_GammaW1,Ln_Ga
mmaW2,GammaW1,GammaW2;     !enthalpy change in the mixing node before waste;


        CompositionWaste(Waste):compWaste, molecompWaste, moleWaterWaste,
moleWaste;             !composition of the waste;
        TemperatureWaste(Waste):tempWaste;
        !temperature of waste;
        PropertyWaste(Waste):propWaste;
        !property of waste;
        heatCapacityWaste(Waste):CpWaste;
        !heat capacity of waste;

Endsets

Data:
        TotalFlowSR=3661,1766,1485;
        compSR=0.016, 0.024, 0.22;
        tempSR=75,65,40;
```

```
        propSR=38,25,7;
!       CpSR=4.2, 4.2, 4.2;

        compFR=0, 0.012;
        tempFR=25,35;
        propFR=3,6;
!       CpFR=4.2,4.2;
        costFR=0.00132,0.00088;

        inflowSK=2718,1993,1127;
        mincompSK=0,0,0;
        maxcompSK=0.013, 0.013, 0.1;
        mintempSK=60,30,25;
        maxtempSK=80,75,65;
        minpropSK=15,10,13;
        maxpropSK=35,25,40;
!       CpSK=4.2, 4.2, 4.2;

!       deltaH_Sink=0,0,0;                              !assumed to be zero;
!       deltaH_Waste=0;
!       CpWaste=4.2;

        To=0;                                           !standard
temperature is assumed to be zero;
        costWaste=0.002;                                !assumed value;
        MoleWtWater=18;                                 !unit:   g/mol;
        MoleWtPhenol=94.11;
!       Cp_Water=4.190;                                 !Cp = 4.1855 J/(g·K)
(25 °C) = 4.1855 kJ/(kg·K);

        Constant_R=8.314;                               ! the gas constant
8.314472 J/(K·mol)= 8.314472 kJ/(K·kmol);
        alpha12=2.4395;
        alpha21=-3.2239;
        b12=-2229.9297;
        b21=1046.1246;
Enddata


!objective function: ;
min=MinCost*8000;

MinCost=@sum(Fresh(r):flowFR*costFR)+@sum(Waste(w):inflowWaste*costWaste);
```

```
!constraints;
!1. Mass balance for ith source:;
          @for(TotalflowSource(i):
                              TotalFlowSR(i) =
@sum(flowSink(j):flowSRSK(i,j))+@sum(Waste(w):flowSRWaste(i,w)));
!2. The similar mass balance can be applied for rth fresh source without assign any fresh
to waste:;
          @for(Fresh(r):
                              flowFR(r) = @sum(flowSink(j):flowFRSK(r,j)));
!3.Mass balance for jth sink:;
          @for(flowSink(j):
                              inflowSK(j)=
@sum(Fresh(r):flowFRSK(r,j))+@sum(TotalflowSource(i):flowSRSK(i,j)));
!4. Component material balance for jth sink:;

          @for(flowSink(j):
                              inflowSK(j)*incompSK(j)=
@sum(Fresh(r):flowFRSK(r,j)*compFR(r))+@sum(TotalflowSource(i):flowSRSK(i,j)*
compSR(i)));
!5. If the heat effect of mixing is involved, the heat balance for the jth sink can be
rewritten as:;

          @for(flowSink(j):
                              inflowSK(j)*CpSK(j)*(intempSK(j)-To)
                              = @sum(Fresh(r):flowFRSK(r,j)*CpFR(r)*(tempFR(r)-
To))+@sum(TotalflowSource(i):flowSRSK(i,j)*CpSR(i)*(tempSR(i)-
To))+deltaH_Sink(j));
!Calculating the mole fractions:;

          @for(CompositionFresh(r):


          molecompFR(r)=compFR(r)/MoleWtPhenol/(compFR(r)/MoleWtPhenol+(1-
compFR(r))/MoleWtWater);
                              moleWaterFR(r)=1-compFR(r);

                    );

          @for(CompositionSource(i):


          molecompSR(i)=compSR(i)/MoleWtPhenol/(compSR(i)/MoleWtPhenol+(1-
compSR(i))/MoleWtWater);
                              moleWaterSR(i)=1-molecompSR(i);
```

```
                );

        @for(CompositionSink(j):

        molecompSK(j)=incompSK(j)/MoleWtPhenol/(incompSK(j)/MoleWtPhenol+(1-
incompSK(j))/MoleWtWater);
                        moleWaterSK(j)=1-molecompSK(j);
                );

        @for(CompositionWaste(w):

        molecompWaste(w)=compWaste(w)/MoleWtPhenol/(compWaste(w)/MoleWtPh
enol+(1-compWaste(w))/MoleWtWater);

                        moleWaterWaste(w)=1-molecompWaste(w);

                );

!Calculating heat capacity:;

        @for(heatCapacityFresh(r):


        CpFR(r)=molecompFR(r)*(0.0044*(tempFR(r)+273.15)+0.4685)+moleWaterFR
(r)*(0.0083*(tempFR(r)+273.15)+1.3724);

                );

        @for(heatCapacitySource(i):


        CpSR(i)=molecompSR(i)*(0.0044*(tempSR(i)+273.15)+0.4685)+moleWaterSR
(i)*(0.0083*(tempSR(i)+273.15)+1.3724);

                );

        @for(heatCapacitySink(j):


        CpSK(j)=molecompSK(j)*(0.0044*(intempSK(j)+273.15)+0.4685)+moleWaterS
K(j)*(0.0083*(intempSK(j)+273.15)+1.3724);

                );

        @for(heatCapacityWaste(w):
```

```
        CpWaste(w)=molecompWaste(w)*(0.0044*(tempWaste(w)+273.15)+0.4685)+m
oleWaterWaste(w)*(0.0083*(tempWaste(w)+273.15)+1.3724);

                );

!Calculating heat of mixing:;

!the oringinal heat of mixing should multiply the mole flow rates of sinks or waste;

        @for(deltaEnthalpySink(j):

                        deltaH_Sink(j)=-
Constant_R*moleSink(j)*molecompSK(j)*moleWaterSK(j)*(A12(j)*b12/(molecompS
K(j)+moleWaterSK(j)*A12(j))+A21(j)*b21/(moleWaterSK(j)+molecompSK(j)*A21(j))
);

!Calculate the mole flow rates of sinks;


        moleSink(j)=inflowSK(j)*incompSK(j)/MoleWtPhenol+inflowSK(j)*(1-
incompSK(j))/MoleWtWater;

                        Ln_Gamma1(j)=-
@log(molecompSK(j)+A12(j)*moleWaterSK(j))


        +moleWaterSK(j)*(A12(j)/(molecompSK(j)+A12(j)*moleWaterSK(j))-
A21(j)/(moleWaterSK(j)+A21(j)*molecompSK(j)));

                        Ln_Gamma2(j)=-
@log(moleWaterSK(j)+A21(j)*molecompSK(j))

                                        -
molecompSK(j)*(A12(j)/(molecompSK(j)+A12(j)*moleWaterSK(j))-
A21(j)/(moleWaterSK(j)+A21(j)*molecompSK(j)));

                        Gamma1(j)=@exp(Ln_Gamma1(j));

                        Gamma2(j)=@exp(Ln_Gamma2(j));

                        A21(j)=@exp(alpha21+b21/(intempSK(j)+273.15));

                        A12(j)=@exp(alpha12+b12/(intempSK(j)+273.15));
```

```
                    );

!6.Property balance in the jth sink;

        @for(flowSink(j):
                        inflowSK(j)*inpropSK(j)=
@sum(Fresh(r):flowFRSK(r,j)*propFR(r))+@sum(TotalflowSource(i):flowSRSK(i,j)*p
ropSR(i)));
!7.property is dependent on the temperature and composition;


!       @for(PropertySink(j):
                        inpropSK(j)=
molecompSK(j)*0.133322*2.58*@exp(0.0314*intempSK(j))
                                +(1-molecompSK(j))*0.133322*@exp(20.386-
5132/(intempSK(j)+273.15)));
!8.Sinks composition constrains:;

        @for(CompositionSink(j):

                        incompSK(j)<=maxcompSK(j));

        @for(CompositionSink(j):

                        incompSK(j)>=mincompSK(j));
!9.Sinks temperature constrains:;

        @for(TemperatureSink(j):

                        intempSK(j)<=maxtempSK(j));

        @for(TemperatureSink(j):

                        intempSK(j)>=mintempSK(j));

!10. Sinks properties constrains:;

        @for(PropertySink(j):

                        inpropSK(j)<=maxpropSK(j));

        @for(PropertySink(j):

                        inpropSK(j)>=minpropSK(j));

!11.Mass balance for the waste:;
```

```
	@for(Waste(w):
				inflowWaste(w)= @sum(TotalflowSource(i):flowSRWaste(i,w)));
!12. Component material balance for waste:;

	@for(Waste(w):
				inflowWaste(w)*compWaste(w)=
@sum(TotalflowSource(i):flowSRWaste(i,w)*compSR(i)));
!13. If the heat effect of mixing is involved, the heat balance for the waste can be
rewritten as:;

	@for(Waste(w):
				inflowWaste(w)*CpWaste(w)*(tempWaste(w)-To)
				=
@sum(TotalflowSource(i):flowSRWaste(i,w)*CpSR(i)*(tempSR(i)-
To))+deltaH_Waste(w));

!Calculating heat of mixing:;
	@for(deltaEnthalpyWaste(w):

				deltaH_Waste(w)=-
Constant_R*moleWaste(w)*molecompWaste(w)*moleWaterWaste(w)*(Aw12(w)*b12/
(molecompWaste(w)+moleWaterWaste(w)*Aw12(w))+Aw21(w)*b21/(moleWaterWast
e(w)+molecompWaste(w)*Aw21(w)));

!!Calculate the mole flow rates of wastes;


	moleWaste(w)=inflowWaste(w)*compWaste(w)/MoleWtPhenol+inflowWaste(w
)*(1-compWaste(w))/MoleWtWater;

				Ln_GammaW1(w)=-
@log(molecompWaste(w)+Aw12(w)*moleWaterWaste(w))


	+moleWaterWaste(w)*(Aw12(w)/(molecompWaste(w)+Aw12(w)*moleWaterW
aste(w))-Aw21(w)/(moleWaterWaste(w)+Aw21(w)*molecompWaste(w)));

				Ln_GammaW2(w)=-
@log(moleWaterWaste(w)+Aw21(w)*molecompWaste(w))

								-
molecompWaste(w)*(Aw12(w)/(molecompWaste(w)+Aw12(w)*moleWaterWaste(w))-
Aw21(w)/(moleWaterWaste(w)+Aw21(w)*molecompWaste(w)));
```

```
                        GammaW1(w)=@exp(Ln_GammaW1(w));

                        GammaW2(w)=@exp(Ln_GammaW2(w));

                        Aw21(w)=@exp(alpha21+b21/(tempWaste(w)+273.15));

                        Aw12(w)=@exp(alpha12+b12/(tempWaste(w)+273.15));


                );
!14.property load in the waste stream;
        @for(Waste(w):
                        inflowWaste(w)*propWaste(w)=
@sum(TotalflowSource(i):flowSRWaste(i,w)*propSR(i)));
!       @for(PropertyWaste(w):
                        propWaste(w)=
molecompWaste(w)*0.133322*2.58*@exp(0.0314*tempWaste(w))
                                        +(1-
molecompWaste(w))*0.133322*@exp(20.386-5132/(tempWaste(w)+273.15)));

        @free(alpha21);
        @free(b12);
        @for(deltaEnthalpySink(j):
                        @free(deltaH_Sink(j));
                        @free(A12(j));
                        @free(A21(j));
                        @free(Ln_Gamma1(j));
                        @free(Ln_Gamma2(j));
                        @free(Gamma1(j));
                        @free(Gamma2(j));
                );
        @for(deltaEnthalpyWaste(w):
                        @free(deltaH_Waste(w));
                        @free(Aw12(w));
                        @free(Aw21(w));
                        @free(Ln_GammaW1(w));
                        @free(Ln_GammaW2(w));
                        @free(GammaW1(w));
                        @free(GammaW2(w));
                );
```

Solvent Extraction coding

The coding used for the optimization of the base case at 5% solvent loss:

```
MAX=SALES-COST;

SALES=B2*COST_OIL+(S1+S2+S3)*COST_SLUDGE;
COST=(M1+M2+M3)*COST_SOLVENT+((Q1+Q2+Q3+QREBOILING)*4*10^-
6)+(QCONDENSING*6*10^-6);!4$/MMBTU AND ASSUME;
COST_BUTANOL=1.54;!1.54$/kg;
COST_MEK=0.75;!0.75$/kg;

COST_SOLVENT=COST_BUTANOL*Y1+COST_MEK*Y2;
COST_OIL=1.75;
COST_SLUDGE=0.5;


!stage 1;

G1=RA+U+M1;
U=100;!kg/hr;
G1=S1+F1;
y1G1*G1=Y1S1*S1+Y1F1*F1; !1 IS FOR BASE OIL;
Y2G1*G1=Y2S1*S1+Y2F1*F1; !2 IS FOR CONTAMINANTS;
Y3G1*G1=Y3S1*S1+Y3F1*F1; !3 IS FOR SOLVENT;
Y1G1+Y2G1+Y3G1=1;
Y1S1+Y2S1+Y3S1=1;
Y1F1+Y2F1+Y3F1=1;

Y1G1*G1=0.85*U;
Y2G1*G1=0.15*U;
Y3G1*G1=M1+RA;

a11=15.69097;
b11=6.519031;
c11=0.4133834;
d11=0.15175;
e11=2.518516;
k11=0.1395698E-04;
l11=3.291565;
m11=1.669866;
n11=0.555E-01;

A22=6.718061;
B22=6.898024;
C22=0.386576;
D22=0.42875E-01;
E22=2.313249;
K22=0;
L22=3.303513;
M22=1.331624;
N22=0.62E-01;

T1<50;!T is temperature in C;
T1>20;
SOR1>1;!r is solvent to oil ratio;
SOR1<5;
```

```
!T=25;
!SOR1=3;
!PERCENT_SLUDGE_REMOVAL1>2;

POL_BUTANOL_1=(a11+b11*(@exp(-c11*SOR1)))+(-d11*T1+e11);!BUTANOL;
PSR_BUTANOL_1=(k11+l11*(@log(m11*SOR1)))-(n11*T1);!BUTANOL;

POL_MEK_1=(a22+b22*(@exp(-c22*SOR1)))+(-d22*T1+e22);!MEK;
PSR_MEK_1=(k22+l22*(@log(m22*SOR1)))-(n22*T1);!MEK;

!POL_1=POL_BUTANOL_1*Y1+POL_MEK_1*Y2;
POL_1<=POL_BUTANOL_1+100*(1-Y1);
POL_1>=POL_BUTANOL_1-100*(1-Y1);
POL_1<=POL_MEK_1+100*(1-Y2);
POL_1>=POL_MEK_1-100*(1-Y2);


!PSR_1=PSR_BUTANOL_1*Y1+PSR_MEK_1*Y2;
PSR_1<=PSR_BUTANOL_1+100*(1-Y1);
PSR_1>=PSR_BUTANOL_1-100*(1-Y1);
PSR_1<=PSR_MEK_1+100*(1-Y2);
PSR_1>=PSR_MEK_1-100*(1-Y2);


SOR1=(RA+M1)/U;
POL_1*U/100=Y1S1*S1;
PSR_1*U/100=Y2S1*S1;
Y3S1*S1=0.05*RA;!5%SOLVENT LOSS;

Q1_BUTANOL=(2.1*U+2.936*(RA+M1))*(T1-20); ! 20C IS ROOM TEMPERATURE THE
UNIT OF Q IS KJ/HR;
Q1_MEK=(2.1*U+2.23*(RA+M1))*(T1-20);
!Q1=Q1_BUTANOL*Y1+Q1_MEK*Y2;

Q1<=Q1_BUTANOL+100000*(1-Y1);
Q1>=Q1_BUTANOL-100000*(1-Y1);
Q1<=Q1_MEK+100000*(1-Y2);
Q1>=Q1_MEK-100000*(1-Y2);

!Stage 2;

T2>20;
T2<50;
SOR2>1;
SOR2<5;

G2=F1+M2+RB;
G2=F2+S2;
Y1G2*G2=Y1F2*F2+Y1S2*S2;
Y2G2*G2=Y2F2*F2+Y2S2*S2;
Y3G2*G2=Y3F2*F2+Y3S2*S2;

Y1G2*G2=Y1F1*F1;
Y2G2*G2=Y2F1*F1;
```

```
Y3G2*G2=Y3F1*F1+M2+RB;

Y1G2+Y2G2+Y3G2=1;
Y1F2+Y2F2+Y3F2=1;
Y1S2+Y2S2+Y3S2=1;



POL_BUTANOL_2=(a11+b11*(@exp(-c11*SOR2)))+(-d11*T2+e11);!BUTANOL;
PSR_BUTANOL_2=(k11+l11*(@log(m11*SOR2)))-(n11*T2);!BUTANOL;

POL_MEK_2=(a22+b22*(@exp(-c22*SOR2)))+(-d22*T2+e22);!MEK;
PSR_MEK_2=(k22+l22*(@log(m22*SOR2)))-(n22*T2);!MEK;

!POL_2=POL_BUTANOL_2*Y1+POL_MEK_2*Y2;
POL_2<=POL_BUTANOL_2+100*(1-Y1);
POL_2>=POL_BUTANOL_2-100*(1-Y1);
POL_2<=POL_MEK_2+100*(1-Y2);
POL_2>=POL_MEK_2-100*(1-Y2);


!PSR_2=PSR_BUTANOL_2*Y1+PSR_MEK_2*Y2;

PSR_2<=PSR_BUTANOL_2+100*(1-Y1);
PSR_2>=PSR_BUTANOL_2-100*(1-Y1);
PSR_2<=PSR_MEK_2+100*(1-Y2);
PSR_2>=PSR_MEK_2-100*(1-Y2);

SOR2=(Y3G2*G2)/((1-Y3F1)*F1);
(POL_2/100)*(1-Y3F1)*F1=Y1S2*S2;
(PSR_2/100)*(1-Y3F1)*F1=Y2S2*S2;
Y3S2*S2=0.05*Y3G2*G2; !5%SOLVENT LOSS;

Q2_BUTANOL=(2.1*Y1F1*F1+2.936*Y3F1*F1)*@ABS(T2-T1)+2.936*(M2+RB)*(T2-
20);
Q2_MEK=(2.1*Y1F1*F1+2.23*Y3F1*F1)*@ABS(T2-T1)+2.23*(M2+RB)*(T2-20);
!Q2=Q2_BUTANOL*Y2+Q2_MEK*Y2;
Q2<=Q2_BUTANOL+100000*(1-Y1);
Q2>=Q2_BUTANOL-100000*(1-Y1);
Q2<=Q2_MEK+100000*(1-Y2);
Q2>=Q2_MEK-100000*(1-Y2);


!Stage 3;

T3>20;
T3<50;
SOR3>1;
SOR3<5;

G3=F2+M3+RC;
G3=F3+S3;
Y1G3*G3=Y1F3*F3+Y1S3*S3;
Y2G3*G3=Y2F3*F3+Y2S3*S3;
```

```
Y3G3*G3=Y3F3*F3+Y3S3*S3;

Y1G3*G3=Y1F2*F2;
Y2G3*G3=Y2F2*F2;
Y3G3*G3=+Y3F2*F2+RC+M3;


Y1G3+Y2G3+Y3G3=1;
Y1F3+Y2F3+Y3F3=1;
Y1S3+Y2S3+Y3S3=1;



POL_BUTANOL_3=(a11+b11*(@exp(-c11*SOR3)))+(-d11*T3+e11);!BUTANOL;
PSR_BUTANOL_3=(k11+l11*(@log(m11*SOR3)))-(n11*T3);!BUTANOL;

POL_MEK_3=(a22+b22*(@exp(-c22*SOR3)))+(-d22*T3+e22);!MEK;
PSR_MEK_3=(k22+l22*(@log(m22*SOR3)))-(n22*T3);!MEK;

!POL_3=POL_BUTANOL_3*Y1+POL_MEK_3*Y2;
POL_3<=POL_BUTANOL_3+100*(1-Y1);
POL_3>=POL_BUTANOL_3-100*(1-Y1);
POL_3<=POL_MEK_3+100*(1-Y2);
POL_3>=POL_MEK_3-100*(1-Y2);


!PSR_3=PSR_BUTANOL_3*Y1+PSR_MEK_3*Y2;
PSR_3<=PSR_BUTANOL_3+100*(1-Y1);
PSR_3>=PSR_BUTANOL_3-100*(1-Y1);
PSR_3<=PSR_MEK_3+100*(1-Y2);
PSR_3>=PSR_MEK_3-100*(1-Y2);

SOR3=(Y3G3*G3)/((1-Y3F2)*F2);
(POL_3/100)*(1-Y3F2)*F2=Y1S3*S3;
(PSR_3/100)*(1-Y3F2)*F2=Y2S3*S3;
Y3S3*S3=0.05*Y3G3*G3; !5%SOLVENT LOSS;

Q3_BUTANOL=(2.1*Y1F2*F2+2.936*Y3F2*F2)*@ABS(T3-T2)+2.936*(M2+RC)*(T3-
20);!BUTANOL;
Q3_MEK=(2.1*Y1F2*F2+2.23*Y3F2*F2)*@ABS(T3-T2)+2.23*(M2+RC)*(T3-20);
!Q3=Q3_BUTANOL*Y1+Q3_MEK*Y2;
Q3<=Q3_BUTANOL+100000*(1-Y1);
Q3>=Q3_BUTANOL-100000*(1-Y1);
Q3<=Q3_MEK+100000*(1-Y2);
Q3>=Q3_MEK-100000*(1-Y2);

Y2F3*F3<0.03*U; !THIS MEANS THAT THE PERCENT SLUDGE AFTER THE
EXTRACTION UNITS SHOULD BE LESS THAN 3%;

!KG_SLUDGE_REMOVED=Y2S1*S1+Y2S2*S2+Y2S3*S3;
!KG_SLUDGE_REMOVED>6;

SU=Y1F3*F3+Y3F3*F3;!THIS EQUATION SAYS THAT NO CONTAMINANTS GOES INTO
THE DISTILLATION COLUMN;
```

```
Y1SU*SU=Y1F3*F3;
Y3SU*SU=Y3F3*F3;
SU=R1+B1;
Y1SU*SU=Y1R1*R1+Y2B1*R2;
Y3SU*SU=Y3R1*R1+Y3B1*B1;
Y1SU+Y3SU=1;
Y1R1+Y3R1=1;
Y1B1+Y3B1=1;
Y3B1_BUTANOL=2*10^65*Tsu^(-25.29);
Y3B1_MEK=3*10^43*Tsu^(-17.16);
Y3B1=Y3B1_BUTANOL*Y1+Y3B1_MEK*Y2;
Y3R1>0.99;
Tsu<400;!T IN THE COLUMN IN KELVIN, HIGHER THAN 410K THE BASE OIL
STARTS DECOMPOSING AND LOOSES QUALITY;

QCONDENSING1_BUTANOL=1454.32*R1;
QCONDENSING1_MEK=1094.61*R1;
QCONDENSING1=QCONDENSING1_BUTANOL*Y1+QCONDENSING_MEK*Y2;
QCONDENSING1>0;

QREBOILING1_BUTANOL=489156+(-378124-R1*(-1454.32));
QREBOILING1_MEK=335966+(-284598-R1*(-1094.61));
QREBOILING1=QREBOILING1_BUTANOL*Y1+QREBOILING1_MEK*Y2;
QREBOILING1>0;

VDU=B1;
Y1VDU*VDU=Y1B1*B1;
Y3VDU*VDU=Y3B1*B1;
Y1VDU+Y3VDU=1;
VDU=R2+B2;
Y1VDU*VDU=Y1R2*R2+Y1B2*B2;
Y3VDU*VDU=Y3R2*R2+Y3B2*B2;
Y1R2+Y3R2=1;
Y1B2+Y3B2=1;
Y3B2_BUTANOL=-0.0016*Tvdu+0.6;
Y3B2_MEK=-0.0015*Tvdu+0.5511;
Y3B2=Y3B2_BUTANOL*Y1+Y3B2_MEK*Y2;

Y1R2=0;

Y3B2<0.02;
Tvdu<410;!kelvin;
QCONDENSING2_BUTANOL=1664.32*R2;
QCONDENSING2_MEK=1207.74*R2;
QCONDENSING2=QCONDENSING2_BUTANOL*Y1+QCONDENSING2_MEK*Y2;
QCONDENSING2>0;
QREBOILING2_BUTANOL=476755+(-432721-R2*(-1664.31));
QREBOILING2_MEK=336466+(-338166-R2*(-1207.74));
QREBOILING2=QREBOILING2_BUTANOL*Y1+QREBOILING2_MEK*Y2;
QREBOILING2>0;



QCONDENSING=QCONDENSING1+QCONDENSING2;
```

```
QREBOILING=QREBOILING1+QREBOILING2;


R1+R2=R;
R=RA+RB+RC;


@BIN(Y1);
@BIN(Y2);
Y1+Y2=1;
```

The coding used for the optimization of the base case at 10% solvent loss:

```
MAX=SALES-COST;

SALES=B2*COST_OIL+(S1+S2+S3)*COST_SLUDGE;
COST=(M1+M2+M3)*COST_SOLVENT+((Q1+Q2+Q3+QREBOILING)*4*10^-
6)+(QCONDENSING*6*10^-6);!4$/MMBTU AND ASSUME;
COST_BUTANOL=1.54;!1.54$kg;
COST_MEK=0.75;!0.75$/kg;

COST_SOLVENT=COST_BUTANOL*Y1+COST_MEK*Y2;
COST_OIL=1.75;
COST_SLUDGE=0.5;


!stage 1;

G1=RA+U+M1;
U=100;!kg/hr;
G1=S1+F1;
y1G1*G1=Y1S1*S1+Y1F1*F1; !1 IS FOR BASE OIL;
Y2G1*G1=Y2S1*S1+Y2F1*F1; !2 IS FOR CONTAMINANTS;
Y3G1*G1=Y3S1*S1+Y3F1*F1; !3 IS FOR SOLVENT;
Y1G1+Y2G1+Y3G1=1;
Y1S1+Y2S1+Y3S1=1;
Y1F1+Y2F1+Y3F1=1;

Y1G1*G1=0.85*U;
Y2G1*G1=0.15*U;
Y3G1*G1=M1+RA;

a11=15.69097;
b11=6.519031;
c11=0.4133834;
d11=0.15175;
e11=2.518516;
k11=0.1395698E-04;
l11=3.291565;
m11=1.669866;
n11=0.555E-01;
```

```
A22=6.718061;
B22=6.898024;
C22=0.386576;
D22=0.42875E-01;
E22=2.313249;
K22=0;
L22=3.303513;
M22=1.331624;
N22=0.62E-01;

T1<50;!T is temperature in C;
T1>20;
SOR1>1;
SOR1<5;

!T=25;
!SOR1=3;
!PERCENT_SLUDGE_REMOVAL1>2;

POL_BUTANOL_1=(a11+b11*(@exp(-c11*SOR1)))+(-d11*T1+e11);!BUTANOL;
PSR_BUTANOL_1=(k11+l11*(@log(m11*SOR1)))-(n11*T1);!BUTANOL;

POL_MEK_1=(a22+b22*(@exp(-c22*SOR1)))+(-d22*T1+e22);!MEK;
PSR_MEK_1=(k22+l22*(@log(m22*SOR1)))-(n22*T1);!MEK;

!POL_1=POL_BUTANOL_1*Y1+POL_MEK_1*Y2;
POL_1<=POL_BUTANOL_1+100*(1-Y1);
POL_1>=POL_BUTANOL_1-100*(1-Y1);
POL_1<=POL_MEK_1+100*(1-Y2);
POL_1>=POL_MEK_1-100*(1-Y2);


!PSR_1=PSR_BUTANOL_1*Y1+PSR_MEK_1*Y2;
PSR_1<=PSR_BUTANOL_1+100*(1-Y1);
PSR_1>=PSR_BUTANOL_1-100*(1-Y1);
PSR_1<=PSR_MEK_1+100*(1-Y2);
PSR_1>=PSR_MEK_1-100*(1-Y2);


SOR1=(RA+M1)/U;
POL_1*U/100=Y1S1*S1;
PSR_1*U/100=Y2S1*S1;
Y3S1*S1=0.1*(RA+M1);!10%SOLVENT LOSS;

Q1_BUTANOL=(2.1*U+2.936*(RA+M1))*(T1-20); ! 20C IS ROOM TEMPERATURE THE
UNIT OF Q IS KJ/HR;
Q1_MEK=(2.1*U+2.23*(RA+M1))*(T1-20);
!Q1=Q1_BUTANOL*Y1+Q1_MEK*Y2;

Q1<=Q1_BUTANOL+100000*(1-Y1);
Q1>=Q1_BUTANOL-100000*(1-Y1);
Q1<=Q1_MEK+100000*(1-Y2);
Q1>=Q1_MEK-100000*(1-Y2);
```

```
!Stage 2;

T2>20;
T2<50;
SOR2>1;
SOR2<5;

G2=F1+M2+RB;
G2=F2+S2;
Y1G2*G2=Y1F2*F2+Y1S2*S2;
Y2G2*G2=Y2F2*F2+Y2S2*S2;
Y3G2*G2=Y3F2*F2+Y3S2*S2;

Y1G2*G2=Y1F1*F1;
Y2G2*G2=Y2F1*F1;
Y3G2*G2=Y3F1*F1+M2+RB;

Y1G2+Y2G2+Y3G2=1;
Y1F2+Y2F2+Y3F2=1;
Y1S2+Y2S2+Y3S2=1;



POL_BUTANOL_2=(a11+b11*(@exp(-c11*SOR2)))+(-d11*T2+e11);!BUTANOL;
PSR_BUTANOL_2=(k11+l11*(@log(m11*SOR2)))-(n11*T2);!BUTANOL;

POL_MEK_2=(a22+b22*(@exp(-c22*SOR2)))+(-d22*T2+e22);!MEK;
PSR_MEK_2=(k22+l22*(@log(m22*SOR2)))-(n22*T2);!MEK;

!POL_2=POL_BUTANOL_2*Y1+POL_MEK_2*Y2;
POL_2<=POL_BUTANOL_2+100*(1-Y1);
POL_2>=POL_BUTANOL_2-100*(1-Y1);
POL_2<=POL_MEK_2+100*(1-Y2);
POL_2>=POL_MEK_2-100*(1-Y2);


!PSR_2=PSR_BUTANOL_2*Y1+PSR_MEK_2*Y2;

PSR_2<=PSR_BUTANOL_2+100*(1-Y1);
PSR_2>=PSR_BUTANOL_2-100*(1-Y1);
PSR_2<=PSR_MEK_2+100*(1-Y2);
PSR_2>=PSR_MEK_2-100*(1-Y2);

SOR2=(Y3G2*G2)/((1-Y3F1)*F1);
(POL_2/100)*(1-Y3F1)*F1=Y1S2*S2;
(PSR_2/100)*(1-Y3F1)*F1=Y2S2*S2;
Y3S2*S2=0.1*Y3G2*G2; !10%SOLVENT LOSS;

Q2_BUTANOL=(2.1*Y1F1*F1+2.936*Y3F1*F1)*@ABS(T2-T1)+2.936*(M2+RB)*(T2-
20);
Q2_MEK=(2.1*Y1F1*F1+2.23*Y3F1*F1)*@ABS(T2-T1)+2.23*(M2+RB)*(T2-20);
!Q2=Q2_BUTANOL*Y2+Q2_MEK*Y2;
Q2<=Q2_BUTANOL+100000*(1-Y1);
Q2>=Q2_BUTANOL-100000*(1-Y1);
```

```
Q2<=Q2_MEK+100000*(1-Y2);
Q2>=Q2_MEK-100000*(1-Y2);


!Stage 3;

T3>20;
T3<50;
SOR3>1;
SOR3<5;

G3=F2+M3+RC;
G3=F3+S3;
Y1G3*G3=Y1F3*F3+Y1S3*S3;
Y2G3*G3=Y2F3*F3+Y2S3*S3;
Y3G3*G3=Y3F3*F3+Y3S3*S3;

Y1G3*G3=Y1F2*F2;
Y2G3*G3=Y2F2*F2;
Y3G3*G3=+Y3F2*F2+RC+M3;


Y1G3+Y2G3+Y3G3=1;
Y1F3+Y2F3+Y3F3=1;
Y1S3+Y2S3+Y3S3=1;



POL_BUTANOL_3=(a11+b11*(@exp(-c11*SOR3)))+(-d11*T3+e11);!BUTANOL;
PSR_BUTANOL_3=(k11+l11*(@log(m11*SOR3)))-(n11*T3);!BUTANOL;

POL_MEK_3=(a22+b22*(@exp(-c22*SOR3)))+(-d22*T3+e22);!MEK;
PSR_MEK_3=(k22+l22*(@log(m22*SOR3)))-(n22*T3);!MEK;

!POL_3=POL_BUTANOL_3*Y1+POL_MEK_3*Y2;
POL_3<=POL_BUTANOL_3+100*(1-Y1);
POL_3>=POL_BUTANOL_3-100*(1-Y1);
POL_3<=POL_MEK_3+100*(1-Y2);
POL_3>=POL_MEK_3-100*(1-Y2);


!PSR_3=PSR_BUTANOL_3*Y1+PSR_MEK_3*Y2;
PSR_3<=PSR_BUTANOL_3+100*(1-Y1);
PSR_3>=PSR_BUTANOL_3-100*(1-Y1);
PSR_3<=PSR_MEK_3+100*(1-Y2);
PSR_3>=PSR_MEK_3-100*(1-Y2);

SOR3=(Y3G3*G3)/((1-Y3F2)*F2);
(POL_3/100)*(1-Y3F2)*F2=Y1S3*S3;
(PSR_3/100)*(1-Y3F2)*F2=Y2S3*S3;
Y3S3*S3=0.1*Y3G3*G3; !10%SOLVENT LOSS;

Q3_BUTANOL=(2.1*Y1F2*F2+2.936*Y3F2*F2)*@ABS(T3-T2)+2.936*(M2+RC)*(T3-
20);!BUTANOL;
```

```
Q3_MEK=(2.1*Y1F2*F2+2.23*Y3F2*F2)*@ABS(T3-T2)+2.23*(M2+RC)*(T3-20);
!Q3=Q3_BUTANOL*Y1+Q3_MEK*Y2;
Q3<=Q3_BUTANOL+100000*(1-Y1);
Q3>=Q3_BUTANOL-100000*(1-Y1);
Q3<=Q3_MEK+100000*(1-Y2);
Q3>=Q3_MEK-100000*(1-Y2);

Y2F3*F3<0.03*U; !THIS MEANS THAT THE PERCENT SLUDGE AFTER THE
EXTRACTION UNITS SHOULD BE LESS THAN 3%;

!KG_SLUDGE_REMOVED=Y2S1*S1+Y2S2*S2+Y2S3*S3;
!KG_SLUDGE_REMOVED>6;

SU=Y1F3*F3+Y3F3*F3;!THIS EQUATION SAYS THAT NO CONTAMINANTS GOES INTO
THE DISTILLATION COLUMN;
Y1SU*SU=Y1F3*F3;
Y3SU*SU=Y3F3*F3;
SU=R1+B1;
Y1SU*SU=Y1R1*R1+Y2B1*R2;
Y3SU*SU=Y3R1*R1+Y3B1*B1;
Y1SU+Y3SU=1;
Y1R1+Y3R1=1;
Y1B1+Y3B1=1;
Y3B1_BUTANOL=2*10^65*Tsu^(-25.29);
Y3B1_MEK=3*10^43*Tsu^(-17.16);
Y3B1=Y3B1_BUTANOL*Y1+Y3B1_MEK*Y2;
Y3R1>0.99;
Tsu<400;!T IN THE COLUMN IN KELVIN, HIGHER THAN 410K THE BASE OIL
STARTS DECOMPOSING AND LOOSES QUALITY;

QCONDENSING1_BUTANOL=1454.32*R1;
QCONDENSING1_MEK=1094.61*R1;
QCONDENSING1=QCONDENSING1_BUTANOL*Y1+QCONDENSING_MEK*Y2;
QCONDENSING1>0;

QREBOILING1_BUTANOL=489156+(-378124-R1*(-1454.32));
QREBOILING1_MEK=335966+(-284598-R1*(-1094.61));
QREBOILING1=QREBOILING1_BUTANOL*Y1+QREBOILING1_MEK*Y2;
QREBOILING1>0;

VDU=B1;
Y1VDU*VDU=Y1B1*B1;
Y3VDU*VDU=Y3B1*B1;
Y1VDU+Y3VDU=1;
VDU=R2+B2;
Y1VDU*VDU=Y1R2*R2+Y1B2*B2;
Y3VDU*VDU=Y3R2*R2+Y3B2*B2;
Y1R2+Y3R2=1;
Y1B2+Y3B2=1;
Y3B2_BUTANOL=-0.0016*Tvdu+0.6;
Y3B2_MEK=-0.0015*Tvdu+0.5511;
Y3B2=Y3B2_BUTANOL*Y1+Y3B2_MEK*Y2;

Y1R2=0;
```

```
Y3B2<0.02;
Tvdu<410;!kelvin;
QCONDENSING2_BUTANOL=1664.32*R2;
QCONDENSING2_MEK=1207.74*R2;
QCONDENSING2=QCONDENSING2_BUTANOL*Y1+QCONDENSING2_MEK*Y2;
QCONDENSING2>0;
QREBOILING2_BUTANOL=476755+(-432721-R2*(-1664.31));
QREBOILING2_MEK=336466+(-338166-R2*(-1207.74));
QREBOILING2=QREBOILING2_BUTANOL*Y1+QREBOILING2_MEK*Y2;
QREBOILING2>0;



QCONDENSING=QCONDENSING1+QCONDENSING2;
QREBOILING=QREBOILING1+QREBOILING2;


R1+R2=R;
R=RA+RB+RC;


@BIN(Y1);
@BIN(Y2);
Y1+Y2=1;
```

Fitted Simulation Data

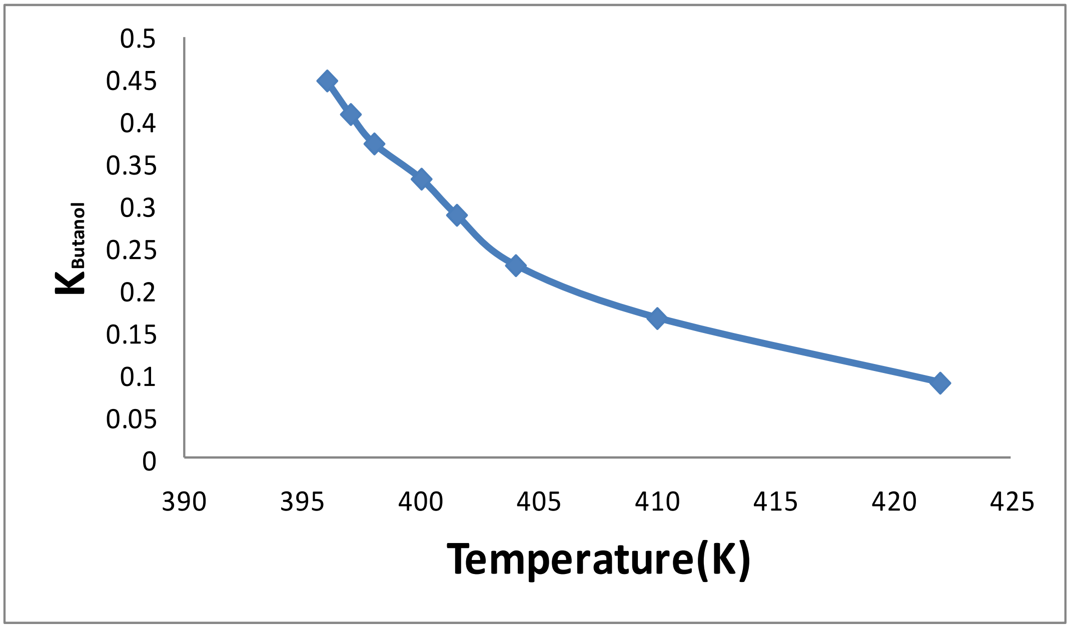

Figure 5.6: Butanol Fitted K value versus atmospheric column temperature

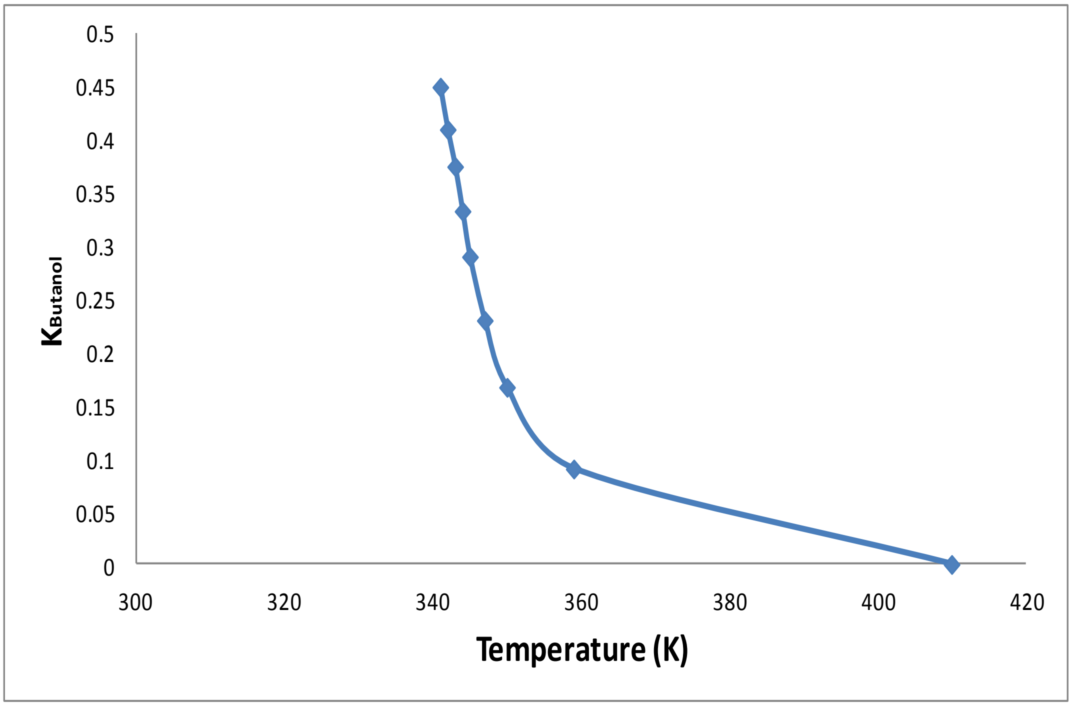

Figure 5.7: Butanol Fitted K value versus vacuum column temperature

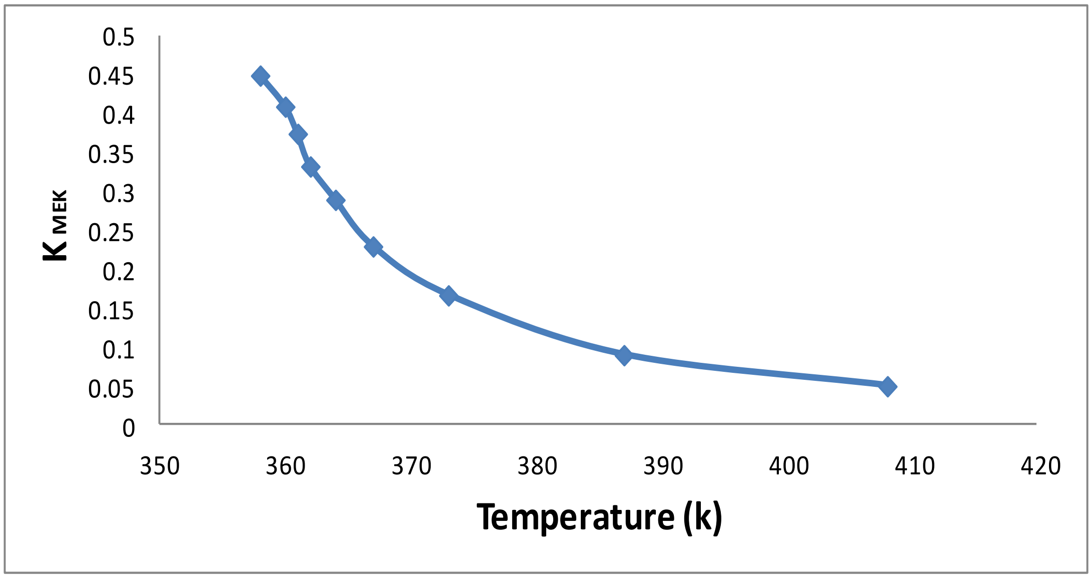

Figure 5.8: MEK Fitted K value versus atmospheric column temperature

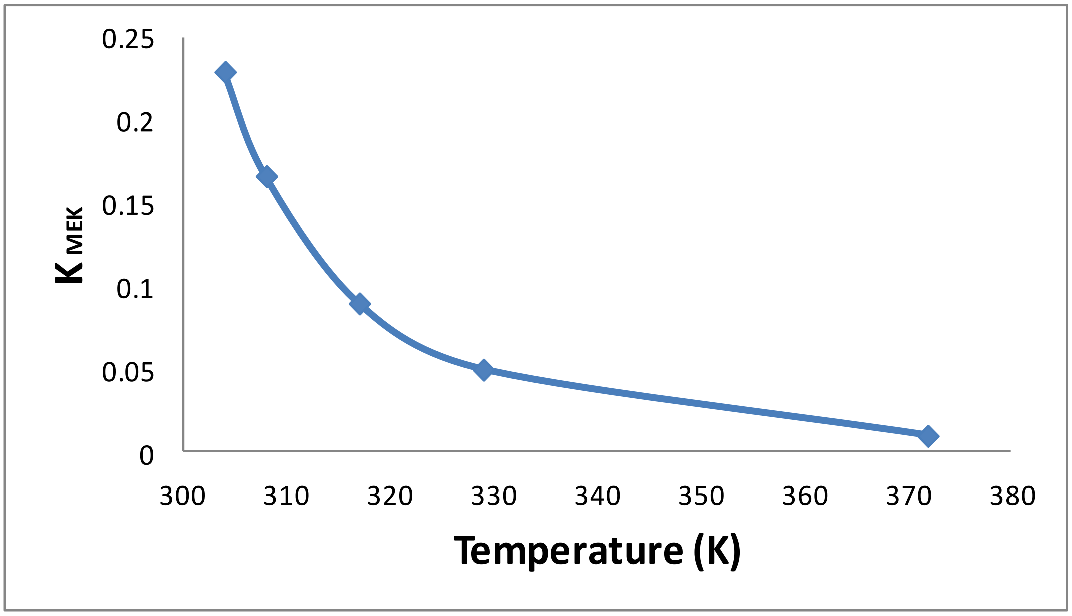

Figure 5.9: MEK Fitted K value versus vacuum column temperature

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