Giovanni Luigi Villanti

Optimization of Regeneration Process of Waste Lubricant Oil by Liquid-Liquid extraction

Master Thesis in the scientific area of Chemical Engineering, submitted to the Department of Chemical Engineering, Faculty of Science and Technology, University of Coimbra

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ABSTRACT

Lubricating oils are one of the most important fluids used for the correct operation of almost all engines and machines. They play a fundamental role in order to avoid friction and wear, and transfer of heat generated between metallic surfaces. After its use, the lubricant must be replaced because its degradation and contamination by water, salts, metals, carbonaceous compounds, etc. diminish their properties. The used oil may be a serious environmental problem if not properly handled and treated. The most important methods for the recycling of used oil making it a valuable product involve re-refining processes that can be performed by several technologies.

The purpose of this study was to investigate the effects of some variables on the solvent extraction process, in order to optimize them in the liquid-liquid extraction for used lubricants. The performance of two solvents, methyl ethyl ketone (MEK) and 1-butanol, was evaluated. For both solvents were tested different solvent-oil ratios from 1:1 to 6:1, varying also the concentration of KOH, used as flocculant agent, and the mixing time. A full factorial design was applied for studying the effect of the process variables on the Yield, percentage of sludge removal (PSR) and percentage of oil loss (POL). The data obtained were then analyzed using the response surface methodology to find the optimal conditions. The best extraction results were found for 1-butanol at a ratio of 6:1 and a KOH concentration of 4 g/L. The responses obtained with MEK showed a similar trend in terms of yield and oil loss.

The physicochemical properties of the regenerated oil were greatly improved comparing with those of the original oil (used oil) demonstrating thus the effectiveness of the process.

Globally it was concluded that the extraction with organic solvents could be an interesting route to regenerate waste oil, while for scaling-up this process to industrial scale the optimal conditions found out in this work may have to be shifted for economic reasons.

RESUMO

Os óleos lubrificantes são fundamentais para o correto funcionamento de motores e máquinas. Estes desempenham um papel crucial de modo a evitar o atrito, o desgaste e atuam como agente de transferência de calor gerado entre superfícies metálicas. Após a sua utilização, o lubrificante deve ser substituído devido à sua degradação e contaminação com água, sais, metais, compostos carbonáceos, etc. que degradam as suas propriedades lubrificantes. O óleo usado pode ser um problema ambiental grave se não for devidamente manuseado e tratado. Os métodos mais importantes para o tratamento do óleo usado envolvem processos de regeneração que podem ser implementados com recurso a várias tecnologias.

O objetivo deste estudo foi investigar o efeito de algumas variáveis operatórias no processo de extração por solvente, de modo a obter as condições ótimas. Foi testado o desempenho de dois solventes, metil-etil-cetona (MEK) e 1-butanol. Para ambos os solventes foram testadas as razões solvente:óleo usado entre 1:1 a 12:1, variando também a concentração de KOH, usado como agente floculante, e o tempo de mistura. Para estudar o efeito das variáveis do processo sobre o rendimento, percentagem de remoção de lamas (PSR) e percentagem de perda de óleo (POL) foi utilizado um desenho de experiências com recurso a um *full factorial*. Os dados obtidos foram analisados utilizando a metodologia de superfície de resposta para encontrar as condições ótimas. Os melhores resultados foram encontrados para a extração com 1-butanol numa razão 6:1 e 4 g/L de KOH. As respostas obtidas com o MEK mostraram uma tendência semelhante, em termos de rendimento e de perda de óleo.

As propriedades físico-químicas do óleo de base regenerado foram significativamente melhoradas em comparação com as do óleo usado original, demonstrando assim a eficácia do processo.

Globalmente, conclui-se que a extração com solventes orgânicos pode ser uma via interessante para regenerar o óleo usado. Contudo, na fase de *scaling up* para a escala industrial as condições ótimas encontradas no presente trabalho podem ter de ser ligeiramente alteradas por razões económicas.

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ABBREVIATIONS

API	American Petroleum Institute (USA)
CCD	Central composite design
CR	Critical solvent-oil ratio
EDXRF	Energy Dispersive X-Ray Fluorescence
EO	Ethylene Oxide
FDA	Food and Drug Administration (USA)
FTIR	Fourier Transform Infrared Spectroscopy
IFP	Institut Français du Petrole
ISO	International Organization for Standardization
NMP	N-methyl-2-pyrrolidone
MEK	Methyl Ethyl Ketone
MIBK	Methyl Isobutyl Ketone
PAG	Polyalkylene Glycol
PAH	Polycyclic Aromatic Hydrocarbon
PAO	Polyalphaolefin
PCB	Polychlorinated Biphenyl
POL	Percentage of oil loss
PSR	Percentage of Sludge Removal
SOR	Solvent:Oil ratio
TAN	Total Acid Number
ULO	Used Lubricating Oil
VI	Viscosity Index

1. INTRODUCTION

The main driving force that sustain the petroleum industry is the constant request for liquid fuel products such as gasoline, kerosene and diesel fuel. Nevertheless the petroleum industry is one of the most profitable business adding in the market other product such as lubricant oils, waxes and asphalt. If at the beginning of times the source of lubricants were animal or vegetable oils, after 1890s with the evolution of industry and the trend to use heavier machinery, the demand for mineral oil increased, causing the rise of petroleum as predominant source of lubricants (Speight and Exall 2014). Since 1930 most of lubricant oils have been obtained from crude (Vazquez-Duhalt 1989).

Base oil (main raw material for producing lubricant oils) total worldwide demand was 35 Mt in 1990, and remains stable since then (Mortier et al. 2010). Estimation of regional and global demands for lubricants demonstrated that Western Europe accounts for only 13% of total worldwide demand, while North America and Asia account for 22% and 30%, respectively (Kupareva and Murzin 2013).

Base oils are usually obtained by crude oil refining. However, non-petroleum base oils can also be used in case of special properties are required or where substitution by natural products is desirable.

Lubricants are fluids filled into engines, gearboxes and hydraulic system that are used between two solid surfaces in contact with each other to form a protective film that reduces friction, prevents over-heating, damage and corrosion. The economic importance of lubricants is often underestimated. In developed countries, a rough estimate of the energy losses due to friction and wear can reach 30% of the total energy produced, representing several billion Euros (Shaik 2003).

Lubricants are composed by base oil and chemical additives. Indeed, many properties of the lubricant are enhanced by the addition of specific additives. For example, stability to oxidation and degradation is improved by the addition of antioxidants, whereas other special additives provide the capability of the lubricant to face extreme pressure. Several types and quantities (up to 30 % w/w) of additives are mixed with the base oil according to its specific application. The base fluid acts as the carrier for these additives and therefore must be able to maintain them in solution under all normal working conditions (Ahmed and Nassar 2009).

During lubricants lifetime in service several changes can occur both in their composition and structure due to degradation and contamination by a number of components. The nature of these contaminants is closely related to the work environment of the oils. Most common components that are present in waste lubricant oils are iron and steel particles, copper, lead, zinc, barium and cadmium from metal surfaces, sulphur and water. In addition, the organic constituents of lubricating oil will also undergo changes and produce undesirable contaminants. Therefore, the indiscriminate disposal of waste lubricant oils into the environment can cause serious pollution and negative impacts in ecosystems.

Indeed, waste oil is a very dangerous polluting product, since it may contain polynuclear aromatic hydrocarbons (PAH), well known for his high carcinogenicity, and high concentrations of heavy metals, such as Pb, Zn, Cu, Cr, Ni and Cd (Vazquez-Duhalt 1989).

The major sources of waste oil contamination are automotive traffic and industrial activity. Thus, the correct disposal and resource preservation are priorities that dictate the expansion of the regeneration of used lubricant oils.

Due to high lube oil consumption various countries have designed their own management systems for waste oil disposal and treatment. Waste oils can be recovered, following tight regulations which give priority to the regeneration process. The contaminants are removed and the undamaged hydrocarbons are re-refined through suitable technologies to produce base oils.

An economically and environmentally analysis suggest as preferred disposal route the regeneration of the waste oil for base oil production instead of destructive routes such as incineration (Fiedler 2004). In North America and Europe, as well as in other countries in the world, legislation is being introduced for the regeneration of waste oils, when this is technically feasible.

The environmental and economic advantages indicate that regeneration is becoming more and more desirable. Thus, the regeneration of waste lubricants not only minimizes hazards and reduces waste, but also protects the environment as well as conserves energy and natural resources (Fan 2010). However, many conventional technologies used today may create other environmental problems, such as inefficient use of energy and chemicals and the generation of harmful waste during the process.

Solvent extraction is one of the cheapest and efficient processes for waste oil regeneration. It allows to separate reactive components, such as unsaturated hydrocarbons and other contaminants from the waste oil, in order to improve the physicochemical properties of the oil.

This work aims to investigate the optimal extraction conditions using organic solvents for the precipitation of contaminants in waste oils. This is the first regeneration step to obtain base oil suitable for the production of new lubricant oils.

The work will be organized as follow: a theoretical introduction at lubricants and lubrication in Chapter 2, to illustrate the conceptual features of lubricant oils, their physicochemical properties, main contaminants arise during use and decline of its properties. In Chapter 3 is presented the state of the art of the solvent extraction process applied in waste oils and the general regeneration technologies, focusing in the extraction process. The adopted experimental methodology and the procedures followed in this work will be discussed in Chapter 4. Finally, in Chapter 5 the results will be presented and discussed.

2. LUBRICANT OILS

The surface of metals and alloys consists of several irregularities and deviations, naturally created as a result of the manufacturing process. A large amount of energy and material loss is caused by the friction and wear due to the surfaces roughness (Bhushan 2001). Lubricants are essential elements used to improve the operating efficiency and reduce loss in energy and materials almost for all modern industries from manufacturing to space program (DellaCorte and Edmonds 2009).

The main function of lubricants is to reduce and minimize wear and friction. Others include the reduction of noise and vibration resulting from friction between two sliding metal surfaces and the cleaning action to prevent potentially harmful products. Another function of lubricants is to act as heat transfer medium, to prevent thermal runaway and dissipate the heat generated during operation. Lubricants are able to protect engines and machines from rust and corrosion as a result of oxidation. Last but not least lubricants can be used to transfer energy into a closed system, such as hydraulic system, transmission and circulating system (Speight and Exall 2014).

Depending on the application, lubricants with different properties can be formulated and classified into two major groups: 1) automotive lubricants and 2) industrial lubricants. More than 60% of total demand around the world are used for vehicles (Fan 2010).

2.1. BASE OILS

The primary element of lubricants is base oil. Its origin can be mineral, when is obtained by the distillation of the crude, synthetic if produced by chemical synthesis or biologic if it is obtained from natural resources such as fats, waxes and vegetables. In this work mineral and synthetic oils will be presented.

Different base oils are available, which can be classified according to their physical or chemical properties. A classification system has been developed by the American Petroleum Institute (API), where mineral and synthetic oils are subdivided in five different groups, according to composition, viscosity index and sulfur content, as shown in Table 2.1.

Table 2.1: Base Oil Categories according to the American Petroleum Institute

	Base Oil Category	**Sulfur (%)**		**Saturates**	**Viscosity Index**
Mineral	**Group I (solvent refined)**	> 0,03	and/or	<90	80 to 120
	Group II (hydrotreated)	< 0,03	and	>90	80 to 120
	Group III (hydrocracked)	< 0,03	and	>90	> 120
Synthetic	**Group IV**	Poly-alpha-olefins synthetic lubricants*			
	Group V	All other base oils not included in Groups I to IV			

Source API 1509 2012

Group I base oils contain higher amounts of sulfur (> 0.03 %) than Group II. In addition, they are produced by two different processes: Group I is obtained by solvent refining and Group II by hydrotreatment. Group III is highly refined mineral oil obtained through hydrocraking, with higher values of viscosity index. Group IV is reserved for poly-alpha-olefins and Group V includes all other base oils not included in Groups I to IV.

2.1.1. MINERAL OILS

Base oil is typically defined as oil with a boiling point range between 300°C and 565°C, composed by hydrocarbons with chains with 18 to 40 carbon atoms. Depending on the chemical structure and composition of its constituent molecules, this oil is classified paraffinic, naphtenic or aromatic (Speight and Exall 2014). Many organic compounds present in crude oil incorporate other elements, sometimes within ring structures or as functional groups attached to the hydrocarbon structure. Those compounds are for example organosulphur, which ones are much more predominant than nitrogen- and oxygen-containing molecules. The crude oil could contain also very high molecular weight resins and asphaltenes which include a variety of heterocyclic and aromatic structures (Mortier et al. 2010). The chemical composition of crude oil also varies with the geological conditions in the place of extraction, affecting the base oil obtained.

Based on the predominant type of structure in the crude, mineral oils can be classified as paraffinic, naphthenic or aromatic. Lubricants with similar molecular weights can have significant different physicochemical characteristics.

Paraffinic hydrocarbon fraction can be linear or branched, with relatively low densities and viscosities. They show little changes in viscosity with temperature compared to cyclic hydrocarbons. There is significant difference between linear and highly branched paraffinics. For example, linear alkanes have good viscosity/temperature characteristics but they tend to crystallize as wax out of the solution, while highly branched alkanes show an opposite behavior.

Naphthenics contain one or more cyclohexane or cyclopentane rings, or a combination of them. Naphthenics have higher densities and viscosities for their molecular weights compared to alkanes. An advantage of alicyclics over alkanes is that they tend to have low melting points and so do not contribute to wax. However, one disadvantage is that alicyclics have inferior viscosity/temperature characteristics.

Aromatics are cyclic unsaturated hydrocarbons containing one or more benzene rings. Aromatic hydrocarbon compounds are poor in oxidative stability and thermal stability. Thus, they are not suitable to produce lubricant oils by themselves. However, combined with paraffins, benzene rings are able to provide the desirable viscosity and temperature properties (Fan 2010).

The main differences between the three groups of hydrocarbons are summarized in Table 2.2.

Table 2.2: Performance characteristics of mineral base oil components (Totten and Westbrook 2003)

Base Oil Property	Paraffins	Naphthenics	Aromatics
Viscosity Index(VI)	Excellent	Poor-Good	Poor
Pour Point	Poor	Good	Excellent
Oxidation/Thermal Stability	Excellent	Poor-Good	Poor
Solvent for Additives	Poor	Good	Excellent

2.1.2. SYNTHETIC OILS

Synthetic lubricant oils consist of compounds that are produced by chemical synthesis, rather than occurring naturally as petroleum constituents (Rudnick and Shubkin 1993).

There are several application fields for synthetic oils, usually being preferred with respect to mineral oils in systems with severe operating conditions, such as extreme temperature. In general, they provide superior mechanical and chemical properties than those shown by mineral base oils. Synthetic lubricants are found for trucks, automobiles, transmissions in industry, marine applications, as well as aerospace and aviation sectors (Mortier et al. 2010).

Unlike mineral oils derived from crude oil, synthetic lubricants have a well defined molecular structure with well controlled molecular weight distributions, physical properties and chemical characteristics (Lugt 2013). Although synthetic oils are more expensive than crude based lubricants, their enhanced performances are often needed for many applications.

The feedstocks from which synthetic lubricants are made have a uniform and smooth molecular structure, which ensures low friction as lubricant layers slide across one another. Reduced friction increases energy through-put for greater fuel efficiency and power and reduces heat and wear for longer equipment life.

Molecular uniformity helps synthetic oils to resist thinning in heat and thickening in cold, which leads to better protection and secure sealing than refined oils in a wide range of operating temperatures. Field experience has shown that synthetics can have economic benefits when used in place of mineral oils. The benefits fall in five general areas:

- Improved energy efficiency
- Wider operating temperature range
- Increased design ratings
- Reduced maintenance
- Better reliability and safer operation

The most important synthetic lubricants are based on polyalphaolefins (PAO), alkylated aromatics, polyisobutylene, aliphatic diesters, polyesters, polyalkylene glycols (PAG) and phosphate esters (Gunderson and Hart 1962).

However, in 2014 the worldwide demand (around 90%) of synthetic base oils is monopolized by three main components: PAO accounted for 44%, esters with 30% and PAG with 13% (IHS 2015).

The designation polyalphaolefin is derived from the source of this class of base oil, usually α-decene or a mixture of α-olefins containing, in general, a minimum of six and a maximum of twelve carbon atoms. The main advantages of PAO is that because of their molecular shape, they do not crystallize or solidify easily, and are able to remain fluid even at low temperature (Ray et al. 2012). In addition, PAOs have narrow boiling ranges, very low pour points, and viscosity index values higher than 135 for all grades, with a kinematic viscosity higher than 4 $mm^2 s^{-1}$ at 100 °C (Mang et al. 2011).

The organic ester group directly affects the physical properties of a lubricant by lowering the lubricant's volatility and raising the flash point. Strong dipole moments that bind the lubricant together are responsible for these effects. The presence of the ester group also affects other properties, such as thermal stability, hydrolytic stability, solvency, lubricity, biodegradability (Rudnick and Shubkin 1993).

Polyalkylene glycols present a high versatility. The two most important characteristics are the low coefficient of friction and the high polarity. The viscosity can vary depending on the molecular weight of the polymers, and can reach very high values (Harnoy 2003). Other important properties are the low temperature of fluidity, and the reduced tendency to produce wax. PAGs are also fire resistant (Rudnick 2006), and depending on the ratio of ethylene oxide used in their production can be either soluble or insoluble in water. The main disadvantage is represented by their incompatibility with mineral oils.

The advantages of these synthetic oils with respect to base mineral oils and are summarized in Table 2.3.

Table 2.3: Comparison of mineral and synthetic oil base stocks (Robinson 1997)

Synthetic oils	Advantages vs mineral oil	Limiting properties	Applications
PAO	High temperature stability Long life High VI Improved wear protection Low volatility Mineral oil compatibility No wax	Solvency Detergency	Circulating oils Gear lubricants Compressor oils Gas turbine oils Greases Automotive engine oil Aviation hydraulic fluid Aviation greases
Organic esters	High temperature stability Long life Low temperature stability High VI Low volatility Solvency/Detergency	Antirust Hydrolytic stability Paint compatibility Oxidative stability	Circulating oils Compressor oils Gas turbine oils Automotive engine oil Aviation greases
PAG	Water versatility High VI Low temperature fluidity Antirust No wax	Mineral oil compatibility Paint compatibility Oxidation stability	Circulating oils Gear lubricants Hydraulic fluid Compressor oils Brake fluid

2.2. MINERAL BASE OILS PRODUCTION

A diversity of hydrocarbons, wax, aromatics, asphalt and other organic molecules rich in sulfur, oxygen and nitrogen are found in crude oils. Most of these molecules are undesirable in lubricants since they cause instability, color, deposits, which are detrimental to base oil properties. Consequently, they need to be removed by several technologies. Lubricant quality could be easily improved by removing these components. The conventional refining process produces base oils with consistent quality at low cost.

Typically, the production of mineral oils by crude oil refining comprises atmospheric and vacuum distillation, deasphalting, solvent extraction, dewaxing and finishing processes.

Distillation: the primary process for separating the useful fractions from crude oil is distillation. Crude oil is distilled at atmospheric pressure to remove gases, gasoline, naphtha, kerosene and light gas oil. Typically petroleum fractions with boiling points below 350 °C are separated in this step.

Vacuum Distillation: thermal decomposition increasingly occurs at higher temperatures. Further separation by distillation of the atmospheric residue into lubricant base oil is carried out in the vacuum unit.

Deasphalting: the vacuum residue contains recoverable lubricant stock of high viscosity mixed with asphalt and resins. This oil is separated from the asphalt and resins using propane deasphalting precipitation process. The liquid propane is kept close to its critical point and, under these conditions, raising the temperature increases selectivity. The separation takes place in a column, where the de-asphalted oil/propane phase, being lower in density, is taken from the top of the tower and the heavy asphalt phase leaves at the bottom.

Solvent extraction: this operation is used to improve the oxidative stability of base oils and the viscosity/temperature characteristic. The aim of the solvent is to dissolve only the undesired components such as the aromatic fractions. In new plants, the solvent often used is N-methylpyrrolidone due to its low toxicity and low solvent/oil ratios, allowing significant energy savings (Sequeira 1994).

Solvent de-waxing: the refined paraffinic oil contains waxes which crystallize at low temperature, reducing the viscosity/temperature properties and increasing the pour point. The wax is removed by solvent dewaxing in order to produce lubricating oil that will not crystallize at low temperature. Commercial solvents in use include propane, methyl isobutyl ketone and also mixed solvents such as methyl ethyl ketone/toluene or methylene dichlo- ride/dichloroethane (Mortier et al. 2010).

Finishing: trace impurities can remain in the base oil, being necessary a finishing step to improve color, oxidation or thermal stability. Most used finishing processes are hydrotreatment or adsorbent clay. The hydrofinishing step is carried out by reacting oil with hydrogen in a fixed bed reactor in the presence of a selective catalyst (cobalt/molybdenum).

2.3. PHYSICOCHEMICAL PROPERTIES OF LUBRICANTS

Different crude oils and refining processes produce base oils with distinct characteristics that must be controlled to assure the production of lubricants that meet machinery requirements (Speight and Exall 2014). Typically determined base oil properties are viscosity, viscosity index, density, color, total acid number (TAN) and saponification number. Elemental analysis and FTIR will also be discussed in the subsequent chapters.

2.3.1. VISCOSITY

Viscosity measures the internal friction within a liquid, reflecting the way molecules interact to resist motion. Viscosity and its dimensions are best explained with the model of parallel layers of fluid. If a shearing force acts, it will displace the layers of fluid on its direction. The upper layers, near the applied shear, move more rapidly than the lower ones because molecular forces act to resist movement between the layers. The difference in velocity between two given fluid layers, related to their linear displacement, is referred to as the shear rate S. This velocity gradient is proportional to the shear stress τ. The proportionality constant η is called dynamic viscosity, and expressed by Eq. (2.1):

$$\eta = \frac{\tau}{S}\ [cP] \tag{2.1}$$

The dynamic viscosity corresponds to these forces that create the resistance to shearing. The relationship between dynamic viscosity and specific gravity is referred to as kinematic viscosity (ν), as shown in Eq.(2.2).

$$\nu = \frac{\eta}{\rho}\ [mm^2/s]\ or\ [cSt] \tag{2.2}$$

The viscosity is one of the most important lubricant properties, influencing the ability of the oil to form a film and minimize friction and wear.

2.3.2. VISCOSITY INDEX

The viscosity index (VI) describes the change of viscosity with the temperature. A low VI indicates a relatively high rate of change of viscosity with temperature, whereas a high VI indicates the opposite. This property is strictly dependent on the composition of the oil. For example, an oil with high naphthenic content would show a greater rate of change in viscosity with respect to a paraffinic one.

The VI is obtained by the measurement of the kinematic viscosity at 40°C and at 100°C, as illustrated in Figure 2.1, and can be calculated according to Eq.(2.3)

$$VI = \frac{L - U}{L - H} \times 100 \tag{2.3}$$

where L is the viscosity at 40ºC of a standard naphthenic oil whose temperature has a high influence on viscosity, assigned as 0 VI. H is the viscosity at 100ºC of a paraffinic oil, whose temperature has little effect on viscosity, assigned as 100 VI, and U is the viscosity of the oil being considered at 40ºC.

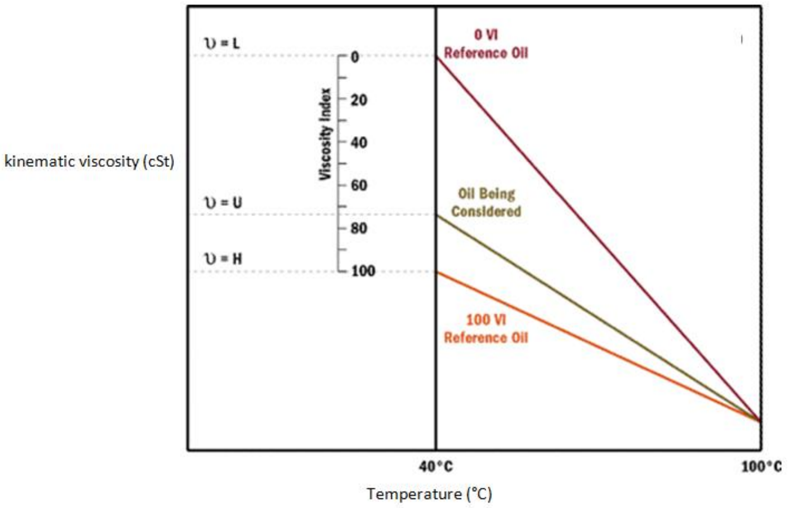


Figure 2.1: Determination of viscosity index

Base oils obtained by the conventional crude refining process can reach VI of about 95. However, higher VI cannot be reached with conventional solvent extraction/solvent dewaxing route, but with other processes, that enable a wider VI range of 95 to 140 (Speight and Exall 2014).

2.3.3. DENSITY AND API GRAVITY

Density is the ratio of the mass per volume of a compound. Knowledge of the density is essential when handling base oils and it can be influenced by the base oil type. Density increases with viscosity, boiling range, aromatic and naphthenic contents, and decreases as isoparaffin levels increase and as the viscosity index increases (Dresel and Mang 2007).

An alternative measure is the API gravity scale where:

$$\text{API gravity} = (141.5/\text{specific gravity}) - 131.5 \tag{2.1}$$

2.3.4. COLOR

Base oils must also meet requirements regarding their color. The color indicates the uniformity of a particular grade or brand. Base oils may have different colors, from colorless to dark brown. Different base oils can have significant differences in color due to the degree of refining finishing process and type of additives. During service life, the overheating, excessive degradation or contaminants such as oxidation products are responsible for changes in color.

Solvent-extracted/solvent-dewaxed stocks will retain some color compounds that can be measured according to ASTM D1500 (Speight and Exall 2014).

2.3.5. TOTAL ACID NUMBER (TAN)

The total acid number (TAN) indicates the presence of acidic components in the oil (ASTM D664). The contact of oxygen with the base oil hydrocarbons can lead to oxidation reactions forming organic acids and other acidic compounds that increase TAN. In new lubricants the presence of certain additives can cause an increase of TAN, while in waste lubricants the TAN is an indicator of the extent of the oil oxidation.

TAN corresponds to the weight (milligrams) of potassium hydroxide required to neutralize 1 g of the materials in the oil that under specific condition will react with KOH.

2.3.6. SAPONIFICATION NUMBER

The saponification number quantifies the amount of saponifiable matter in the oil such as esters or fatty acids, that can occur due to oil degradation or additives. The saponification number is determined by the amount of potassium hydroxide that reacts with 1 g of oil under specified conditions (ASTM D94). An increase in the saponification number indicates an increased propensity to sludge formation (soap). It has been suggested that if the results of other properties are satisfactory, then saponification numbers below 3 mg KOH/g oil may indicates a low content of esters or fatty acids (Totten and Westbrook 2003).

2.3.7. ELEMENTAL ANALYSIS

Elemental analysis is performed to determine specific elements in oil matrix, such as sulfur, chlorine, phosphorus and metals. A common technique is X-ray flourescence (XRF) which has the advantage of being non-destructive, multi-element capability and high level of precision combined with low detection limits (Totten and Westbrook 2003). The XRF use X-rays to bombard the sample, causing the ejection of electrons from the inner shells of the target atoms. Every element produces a specific secondary X-ray spectrum whose intensity is proportional to the element concentration in the sample. Other advantages of this technique are the speed, minimal sample preparation and non-destructive nature. However, XRF instrument involves high investment cost.

2.3.8. FTIR ANALYSIS

Fourier Transform Infrared Spectroscopy (FTIR) is a versatile technique, used to study chemical bonds and functional groups. The IR spectrum contains two types of signals, those usually called "peaks" related to the presence of specific functional groups, and those considered of finger-print. FTIR spectrum allows the detection of different types of lubricants, common contaminants, degradation products and additives.

2.4. ADDITIVES

Base oils cannot satisfy the requirements of high performance lubricants without using modern additive technology. Additives are blended with the base oil to enhance their natural properties and to prevent undesirable effects during service (Rudnick 2003).

Some additives enhance properties that are already present whereas others allow the development of totally new properties to the lubricant. Additives play an important role in increasing the service life of oil, reducing the rate at which undesirable changes in physicochemical characteristics occur (Speight and Exall 2014).

Some lubricant grades (e.g. some compressor or hydraulic lubricants) contain only about 1% of total base oil mass of additives, while others (e.g. some metalworking fluids or gear lubricants) may contain up to 30% (Dresel and Mang 2007).

The most used additives in the lubricants industry and their primary industry are discussed in this section.

- **Viscosity index improvers**

Viscosity modifiers are polymers that maintain the lubricating ability of oils in a wide range of temperatures. In low temperatures, the molecules of polymer adopt a coiled form so that their effect on viscosity is minimized. At high temperatures, the molecules tend to straighten out, and the interaction between these long molecules and the oil produces a proportionally greater thickening effect, as shown in Figure 2.2 (Ahmed and Nassar 2009). These additives increase both the low-temperature viscosity and the high-temperature viscosity of the oil, but to a different degree. Common polymers include polymethacrylates, olefin copolymers, styrene-diene copolymers and styrene-ester copolymers (Rizvi 2014).

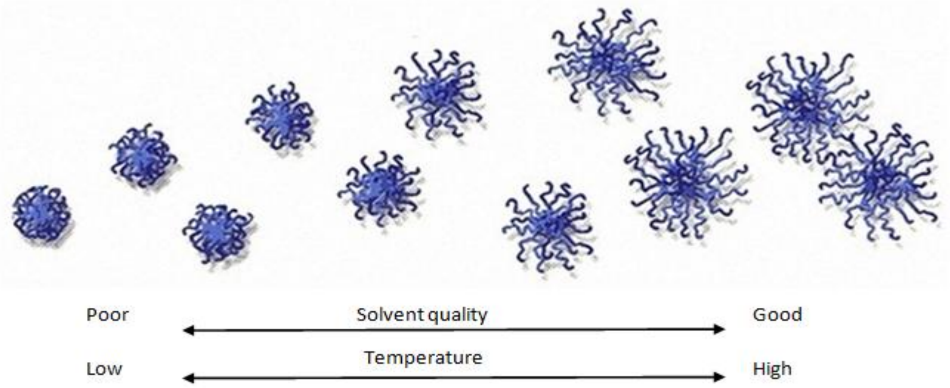


Figure 2.2: Coil expansion model to explain viscosity modifiers mechanism

- **Antiwear and extreme pressure**

Friction during service will cause wear on unprotected metal surfaces (Ludema et al. 1996). As the power of engines has risen, the need for additives to prevent wear has become more important (Ahmed and Nassar 2009). The role of antiwear additives is to prevent the direct contact of two metal parts of the machine reducing wear and increasing machine life. If the system is exposed to very high loads then the lubricant must contain extreme pressure additives. Antiwear and extreme pressure additives present a polar structure that is activated by temperature, reacting with the metal surface to form a protective film, able to slide over the friction surface thus reducing friction and wear of machinery (Speight and Exall 2014).

- **Corrosion and rust inhibitors**

Metal surfaces must be protected against the attack of oxygen, water, acids and bases. Lubricants must protect system from corrosion and rust formation. Corrosion inhibitors are additives that protect nonferrous surfaces, while rust inhibitors protect ferrous surfaces.

Long alkyl chains with a polar functional hear is physically adsorbed or chemically bonded on the metal surface, forming packed hydrophobic layers maintaining a protective film on the surfaces. These types of additives can be either oxygenated inhibitors, essentially carboxylic acids with long organic chains, or nitrogenous inhibitors, fatty amines and their derived products (Speight and Exall 2014; Lugt 2013; Rudnick 2006).

- **Antioxidants**

Lubricant mineral oils in contact with oxygen from the air suffer oxidation reactions and form products such as alkylhydroperoxides, dialkyl peroxides, alcohols, aldehydes, ketones, carboxylic acids and esters. These reactions must be prevented by the use of antioxidant additives that inhibit the oxidation process. Antioxidants play an important role in the protection of metal surfaces since oxidation products are responsible for an increase of the oil viscosity, the formation of sludge and varnish deposits due to further polymerization of these products.

Moreover, the acid character of these compounds increases the danger of corrosion of metallic parts and foaming. The oxidation of hydrocarbons can be described by the free radical mechanism via alkyl and peroxy radicals. The main reaction steps are shown in Figure 2.3.

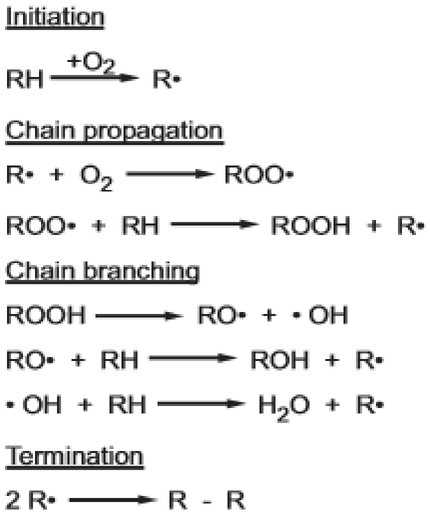


Figure 2.3: Mechanism of oxidative degradation [adapted from (Dresel and Mang 2007) *]*

The role of an antioxidant is to inhibit the radicals that are formed in one of the oxidation steps. Compounds such as alkaline earth phenolates, salicylates, phenol and aromatic amines are used as antioxidants (Speight and Exall 2014).

- **Antifoam agents**

Formation of foam in most lubrication applications is undesirable since it hinders lubrication, promotes oxidation, obstructs narrow passages and reduces the cooling ability. In several applications, there are tendency to agitate the oil that cause foaming. In certain cases even small amounts of foam can be extremely disadvantageous, causing cavitation, as well as insufficient oil transport.

Foam inhibitors (antifoam agents) are additives that reduce the foam-forming tendency of the lubricant. Common additives used to avoid the foam formation include polysiloxanes and styrene ester polymers (Rizvi 2014). These materials act by lowering the surface tension of foam bubbles. The bubbles get attached by the droplets of the defoamant, that cause coalescence into larger bubbles, allowing them to rise to the surface and then collapse, removing the gas from the oil (Ahmed and Nassar 2009).

- **Detergent and dispersants**

Detergent and dispersants prevent the deposition of residues such as sludge and varnish in the metal surfaces, avoiding corrosion and stabilizing the viscosity. They keep in suspension the harmful products and avoid the particles from agglomerating into surfaces.

Detergents and dispersants are in general composed by a large oleophilic hydrocarbon tail and a polar hydrophilic head group. When the additive encounters a target particle, the head groups gets attached to the particle while the tail, forms a layer that is soluble in the oil. This process is usually called peptidization, as shown in Figure 2.4.

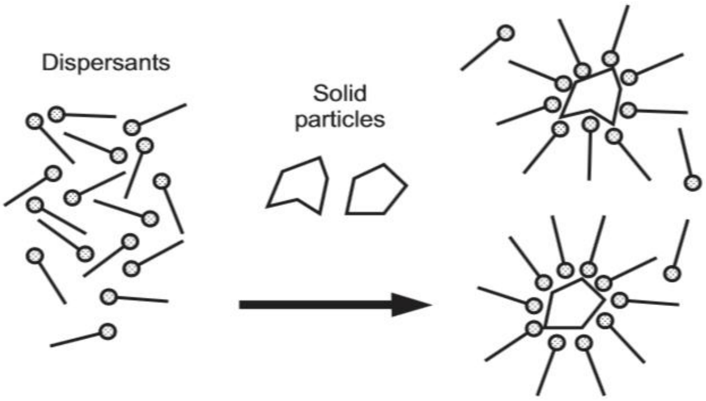


Figure 2.4: Function of dispersants in peptidization process.

Salts of alkaline earth metals, such as calcium and magnesium sulfonates and calcium phenates, are commonly used as detergents to keep engines clean and operate properly. Benzylamides and polymeric succinimides are also usually used to destabilize the adsorption of particles in metal surfaces.

- **Pour point depressants**

The lowest temperature at which the lubricant oils are still able to flow is called pour point. At low temperature the fluidity of the oil is reduced by the formation of wax crystals. Pour point depressants inhibit the formation and agglomeration of wax particles, keeping the oil fluidity. Specific additives maintain the pour point temperature of the lubricating oil below the starting temperature of the engine (Speight and Exall 2014).

Basically there are two different ways to control the wax crystallization phenomenon with pour point depressants. Polymethacrylates are the most widely used depressants and act by delaying the crystal formation to significantly lower temperatures. Alkylaromatic polymers can also be used since they can be adsorbed into the surface of the crystals as they form, in this way they interrupt the lateral crystal growth allowing the oil to flow.

A summary of the main additives is reported in Table 2.4.

Table 2.4: summary of additives and their function, adapted from:(Gergel and Colyer 1992)

Additive	Function	Example
Detergent	Prevent and avoid the deposition of particles. Neutralize the acidic combustion and oxidation products.	Magnesium sulfonates and metallo-organic compound.
Dispersant	Suspend and disperse particles, avoiding the coalescence of sludge	Polymeric succinimides and ash less dispersants.
VI improvers	Improve the VI of the oil even at high temperature.	Acrylates and methacrylates.
Rust and Oxidation inhibitor	Protect metal surfaces with thin films in order to avoid the contact between acids compound and metal.	Ethioxylated alkylpheno and zinc dithiophosphate.
Antifoam	Inhibit the presence of air bubbles in the oil getting attached to them, and promote the coalescence, in order to rise them to the surface to collapse.	Polymethyl siloxanes, silicon type chemicals.
Antiwear	Reduce wear and friction under boundary lubrication conditions.	Esters.
Pour point depressant	Allow the oil to flow even at low temperature, avoiding the formation of wax crystal.	Methacrylates and alkylaromatic polymers.

2.5. USED LUBRICANT OIL CONTAMINANTS

In addition to hydrocarbon compounds (C4 to C50) from the base oil and the additives, waste lubricants also contain unburned fuels, combustion and oxidation products and several contaminants that diminish their performance. The composition of used lubricants collected from engines and machines is highly-dependent on the application field, operating conditions, service lifetime, age of the machines and collecting phase.

Waste oils can be contaminated with several compounds that can be divided into: products of oil deterioration or additives and external contaminants, as shown in Table 2.5.

Table 2.5: Main contaminants of waste lubricant oils (Audibert 2006).

Element	**Conc. (ppm)**	**Contamination from Additives**	**External contamination**
Al	5-30	Grease	Piston and bearings (Al-Sb) wear
B	75-100	Antiwear and high-pressure additives, dispersing antioxidant, friction reducer	Corrosion inhibitor coming from cooling water reducer
Ca	2000-3000	Detergent and antioxidant additives inhibitor- grease	Atmospheric dust and cooling circuit water
Cl	300-600	Antiwear agent, hydraulic fluids, insulators, thermal fluid, extreme-pressure lubricants	-
Cu	25-40	Antioxidant, antiwear additives	Bearing, and wear, corrosion of cupper metals
Fe	50-100	-	Steel and cast iron wear and corrosion
Mg	100-300	Detergent additives-inhibitors	Light alloy wear and corrosion
Mo	5-20	Antiwear and extreme pressure additives	-
N	700-900	Dispersing and antioxidant	-
Ni	3-5	-	Cast iron and allied steel wear and corrosion
Na	50-100	Antirust additive, grease soap	Present as NaCl
P	800-1200	Antiwear, antioxidant, anti-corrosion additives, non flammable hydraulic fluids	Wear and corrosion of cast iron piston skirts and rings
Pb	50	Extreme pressure additives, grease soap	Oil diluition by the fuel and coating bearings
S	0.7-0.9[a)]	Detergent, antiwear extreme pressure and antioxidant additives	-
Si	30-120	Silicon base oil and antifoam additives	Atmospheric dust, wear and corrosion of alloy steel/silica
Zn	1000-1200	Antiwear and antioxidant additives, corrosion inhibitor	-

[a)]- values in percentage (w/w).

In addition of these external contaminants, many products are formed during oil deterioration, such as the sludge, composed by a mixture of oil, water, dust, dirt and carbon particles, varnish that gets deposited on engine parts (Speight and Exall 2014; Audibert 2006).

The main contaminants are listed below (Buckland and Vincent 1974):

- **Combustion products**

Water - the presence of water tends to rust and sludge formation. Combustion is not the only source of water that can derive from condensation from air, infiltrations, antifreeze agents, leak from cooling system, etc.

Soot and carbon - form as result of incomplete combustion, these contaminants are responsible for the changes in the color, turning the oil black.

Fuel - especially during the start-up of engines unburned diesel or gasoline can pass into the oil.

- **Abrasives**

Road dust - little particles of silicates that can pass through the air filter into the engine.

Wear metals - Aluminum, iron and copper are released into the oil due to normal engine wear.

- **Chemical products**

Oxidation products - these organic compounds are corrosive, produced by the oxidation of molecules of the oil at high temperature.

Residual additives

2.6. ENVIRONMENTAL ISSUES

According to the U.S. Environmental Protection Agency (EPA) waste oil is defined as "any oil that has been refined from crude oil, or any synthetic oil, that has been used and as a result of such use is contaminated by physical or chemical impurities”. This definition does not include materials, such as petroleum-based solvents or antifreeze and is based on three criteria: origin, use and contamination (EPA 1997).

The presence of hazardous substances, such as heavy metals, PCBs or other halogen compounds in used oils can cause damage to the environment and public health. Degradation of the quality of air, soil, and ground water can occur if not handled and disposed of in an appropriate manner.

SOIL: waste oil can be dispersed into the soil during motor operation or due to directly deposition in landfills. In general, oil remains on the streets until an external agent such as rain or municipal services clean it. Soil contamination by used lubricating oil from automobiles is a growing concern in many countries, especially in Asian and African continents (Agamuthu et al. 2010). Soils with higher organic content tend to adsorb the oil, preventing its propagation.

However, permeable soils with lower organic content admit migration of the oil to the groundwater (Raymond et al. 1976). Microorganisms are affected by the dispersion of waste oil in the soil. It has been noticed a change in the communities of microorganism that are involved in the nitrogen cycle as well as in the metabolic activity of aerobic microorganisms that oxidize hydrocarbons (Vazquez-Duhalt 1989).

WATER: as previously mentioned, waste oils are generally spilled on the soil, but due to action of rain and runoff water can be rapidly transferred to aquatic environments. In contact with water, lubricants form an impermeable film that avoids the oxygenation of living beings. Physical and chemical changes in the surface film release constituents of waste oils into the environment via volatilization, emulsification, solubilization, partitioning to sediments, photodegradation and biodegradation (CEPA 1994). Changes in the composition of microorganism communities is the main observed effect (Vazquez-Duhalt 1989; Babich and Stotzky 1985). It has been found that used motor oil is one of the most important mutagenic agents in the aquatic environment, causing a significant damage in molluscs, crustaceans and fish (Blumer et al. 1970).

AIR: waste lubricant oils can be as a fuel. The heat of combustion of waste oils is ~12,240 kcal/kg, very similar to petroleum fuels but much less expensive. For this reason, it is used as fuel in industrial boilers, domestic oil burners and waste disposal incinerators. Indiscriminate combustion release harmful compounds to the environment such as metal oxides, dioxins, sulfur oxides, nitro-compounds, hydrochloric acid among others (CEPA 1994). One of the characteristics of all types of burner is that most metal emissions (especially lead) are attached to dust, with particle size lower than 1 μm, and so easy to be inhaled by living organisms (ATSDR 2007).

2.7. LEGISLATION

Waste oils disposal routes depend on the current legislation and the local policies. In several countries, main destinations are recycling by reprocessing to produce secondary products such as fuels, or re-refining to obtain regenerated base oil. Another disposal path is direct burning. In the following sections besides the European legislation will be considered, also the Portuguese and Italian disposal guidelines will be compared.

2.7.1. EUROPEAN LEGISLATION

The Waste Framework Directive 2008/98/EC establishes the regulatory framework of the waste lubricating oils in European Union (EU) countries. It is based on Directive 2006/12/EC, but lays down measures to protect the environment and human health in order to modernize and streamline its provisions.

Especially Article 21 focuses on waste oil, and referring to Article 18 and Article 19, who sets respectively the ban on the mixing of hazardous waste and the labeling of hazardous waste, asserts that Member States shall take the necessary measures to: treat the waste oils in accordance with Articles 4 (Waste hierarchy) and Article 13 (Protection of human health and the environment), collect that waste oils separately. Moreover, if it is economically and technically feasible, waste oils with different characteristics must not be mixed between them and with other type of waste or substances; these specifications are valid if the mixing hampers their treatment.

Other additional measures such as producer responsibility, voluntary agreements, technical requirements or economic instruments can be applied by the Member States, for a better separation, collection of waste oils and their treatment.

Moreover, if waste oils are subject to requirements of regeneration, Member States according to national legislation may prescribe that such waste oils shall be regenerated if technically feasible and, where Articles 11 or 12 of Regulation (EC) No 1013/2006 apply, restrict the transboundary shipment of waste oils from their territory to incineration or co-incineration facilities in order to give priority to the regeneration of waste oils (Directive 2008/98/EC 2008). Member States shall bring into force the laws, regulations and administrative provisions necessary to comply with the Directive by 12 December 2010.

Other directives related to waste lubricating oils that must be referred are the PCBs Directive 96/59/EC and the Incineration of Hazardous Waste Directive 94/67/EC.

Directive 96/59/EC focuses on the disposal of polychlorinated biphenyls and polychlorinated terphenyls, specifying the environmentally safe disposal of PCBs, decontamination or disposal of equipment containing PCBs and/or disposal of used PCBs, considering its total destruction. Member States must compile inventories of equipment containing more than 5 liters of PCBs and adopt a plan for disposal of this equipment.

Directive 94/67/EC aims to reduce the negative effect on air, water and soil pollution due to incineration of hazardous waste to provide measures for preventing or minimizing emissions which may also be harmful to human health. Moreover, it establishes strict operational, technical and licensing criteria for hazardous waste incineration plants.

2.7.2. PORTUGUESE VERSUS ITALIAN REGULATIONS

The legal framework for management and disposal routes of used lubricant oils in Portugal are established by the European directives, transposed into Portuguese legislation by Decreto Lei nº 153/2003 of 11 July amended by Decreto Lei nº 73/2011 of 17 June.

The main points of Decreto Lei nº 153/2003 concerns the fundamental principles of waste oils management, that are the prevention of production in quantity and harmfulness of those waste products and the engagement of best available techniques for collect, transport, storage, treatment and recovery of such waste, in order to minimize and avoid as possible the risks regarding the public health and the environment. In this general provision are excluded waste oils with PCB/PCT concentrations greater than 50 ppm, that are covered by Decreto Lei nº 277/99 of 23 July.

In Decreto Lei nº 153/2003 are listed the hierarchy waste oil management operations: stating at the first place the regeneration, followed by other forms of recycling and then other forms of recovery. As stated in Directive 2008/98/EC, waste oil must be collected separately and those with different characteristics must not be mixed between them or with other waste or substances, if such mixing hampers treatment.

New management responsibilities are introduced, new oil producers are responsible of waste oils circuit, including the correct storage and integration in the circuit of management of waste oils, the producers may also transfer this responsibility to a management entity duly licensed for that purpose. This new entity is responsible for the proper functioning of oils management operations for which is licensed.

The prohibitions for the management listed in Decreto Lei nº 153/2003 are:

- Any discharge of waste oils into surface waters, groundwater, transitional, coastal and marine and drainage systems;
- Any deposit or discharge of waste oils in the soil;
- Any waste oil management operation likely to cause atmospheric emissions exceeding the limits set values in the legislation;
- The energy recovery of waste oils in the food industry
- The mixture of oils of different characteristics or other waste substances or when the mixture in question prevents the processing of waste oils, namely for regeneration purposes.

In Portugal, the management of waste oils is implemented by Sociedade de Gestão Integrada de Óleos Lubrificantes Usados, Lda. (SOGILUB), which financed this work and allowed the accomplishment of the thesis' objectives.

In Italy, the waste oils circuit is coordinated by COOU (Consorzio Obbligatorio Oli Usati), the COOU with its consortium network, operating at national level, ensure the promotion of recycling of hazardous waste through the used oil regeneration treatment, which allows its transformation into new resources available on the market.

In 2010 it was published D.Lgs no.205/10 which implements Directive 2008/98/EC and amending Part IV of D.Lgs no.152/06 relating to waste management. In particular, Art.216-bis of D.Lgs. 152/06 states that used oil should be handled separately, according to the different types; each type of oil must be set to different treatment processes, considering regeneration a priority for the production of lubricating bases (combustion and incineration are the residual alternatives) (D.Lgs 205/10). It is finally sanctioned the general prohibition to mix mineral oils with other wastes or substances.

While is still present the ban of mixing between hazardous and non-hazardous waste, changes the principle to be applied to dangerous waste for which is no longer forbidden the mixing with "other hazardous waste" but not that between "hazardous waste having different hazardous properties".

In particular, the Italian Consortium must develop its activities based on:

- agree with the regeneration companies the technical parameters for the selection of waste oils suitable for regeneration;
- promote the collection of waste oils directed to regeneration;
- send of waste oil to the companies that request it on the basis of the ratio of collected amounts, amounts demands and production capacity authorized;
- the regeneration companies have to pay a fee regarding to the amount of lubricating base obtained per ton of used and its oil quality;
- ensure the combustion of the waste oil that cannot be regenerated but still re-usable, and the disposal of waste which does not find an application, taking into account of anti-pollution regulations.

3. REGENERATION TECHNOLOGIES

In the lube oil industry, the term recycling is very different from re-refining.

Recycling oil or reconditioning oil is commonly related to using filtration to remove insoluble impurities. This method does not remove completely the soluble contaminants, and the application field of the resulting oil is very limited.

Re-refining is a process developed for removing all impurities, both soluble and insoluble, and returns the oil to a quality suitable for automotive. The quality of re-refined oil is usually comparable or sometimes even better than some virgin base oils. Regardless of the feed composition, the overall re-refining process uses the same basic separation techniques that the crude oil refining (Gary and Handwerk 2001; Audibert 2006):

- Filtration, settling, and dehydration or preflash;
- A section of diesel oil recovery;
- Vacuum distillation for the separation of oil fractions, possibly completed with a vacuum residue deasphalting, if the recovery of highly viscous oil is desired;
- Catalytic refining or treatment with clay for finishing of the oil fractions.

3.1. RE-REFINING PROCESSES

The separation of the lubricant base oils from additives, asphalts and other contaminants contained in the used oil has been performed traditionally by distillation and acid/clay treatment. This method involves mixing the use oil with concentrated sulfuric acid that act as an extraction medium for the removal of undesired material from the used oil, forming acid sludge.

However, these traditionally technologies have been banned (Kupareva and Murzin 2013) due to the following problems:

- fouling in the distillation equipment, reducing the operational time of the plant;

- thermal cracking reactions reduce yield and lead to low quality base oils (color, odor, instability, etc.), which is difficult to improve in the final treatment.

- environmental difficulties due to the acid-clay waste disposal, emission of unpleasant odors and water contamination;

More environmentally friendly technologies have been developed as an alternative to the acid/clay treatment. The currently applied technologies can be compared in terms of operating and capital costs, quality of feedstock and products obtained. The technologies described can be divided into the following groups:

1. Solvent extraction process;
2. Hydroprocessing;
3. Vacuum distillation or thin film evaporation and finishing process (solvent extraction or chemical treatment);
4. Thin film evaporation and hydrofinishing;
5. Thermal de-asphalting and hydrofinishing;
6. Solvent extraction and hydrofinishing;

The advantages and drawbacks of the processes currently applied in Europe of re-refining are summarized in Table 3.1. However, in all the processes a pre-treatment is usually required, involving a sequence of simple operation that remove the unwanted contaminants. Large and heavy impurities may be settled from the oil by sedimentation, taking advantage of their solubility in the oil or the difference in density. The oil is filtered before and after being received in the storage tanks, to remove the particles that are bigger than 150/250 µm (Audibert 2006). Water can be removed either by sedimentation or by dehydration or pre-flash, those pre-treatments are carried out in a column for eliminating all compounds more volatile than the diesel oil at the top. In addition of techniques mentioned above, other treatment as filtration and centrifugation can be applied to remove free and emulsified water, suspended matter and heavy impurities (Fan 2010).

Table 3.1: Overview of re-refining processes currently applied in Europe, adapted from (Kupareva and Murzin 2013).

Technology	Feedstock	Investment costs	Product quality	yield,%	Comments
1. Solvent extraction					
MRD process	Process ensures complete preservation of synthetic oils (XHVI,PAO). Feedstock can contain up to 5% of vegetable oils.	Relatively low operating and capital costs.	Good quality base oils: •Quantitative elimination of PAH •a high viscosity index and oxidation stability •high sulfur content	91	Extracts can be used as fuel.
Interline	Mineral motor and industrial oils.	Solvent extraction system operates without extensive heat or pressure. Relatively low operating and capital costs.	Low quality of produced base oil (API I).	79	Production of asphalt modifier.

Table 3.1: Overview of re-refining processes currently applied in Europe, adapted from (Kupareva and Murzin 2013)*(continued).*

Technology	**Feedstock**	**Investment costs**	**Product quality**	**yield,%**	**Comments**
2. Vacuum distillation / Thin film evaporation + finishing process (solvent extraction or chemical treatment)					
Vaxon	Mineral oils and some synthetic lube oils stable in the presence of strong base.	Financially attractive	Medium quality of the produced oil. Final stage does not allow improvement of high quality base oil	65-70	Residue asphalt extender. Finishing process can be chemical treatment or solvent extraction
Eco Huile (Sotulub)	Mineral and some synthetic lube oil, stable in the presence of alkali additive (Antipoll)	No finishing step required, thus investment cost of the process decrease	Low quality base oil produced	82-92	-
3. Hydroprocessing					
Hylube	Used oil from different sources.	The capital investment and operating costs of the process are minimized by eliminating superfluous equipment.	Quite high quality of produced oil (API Group II). Effective dechlorination (PCB's destruction) and desulfurization (less than 0.03 wt.%)	85	Heavy residue-is very stable and is acceptable for asphalt blending
4. TFE+hydrofinishing					
CEP process	Used oil from different sources : industrial and motor mineral and synthetic oils.	High operating and capital costs.	High-quality base oils API Group II.	70	Used catalyst of hydropurification - disposed off-site.
5. TDA + hydrofinishing					
Revivoil	Acceptance of all used motor oil feedstock.	High operating and capital costs.	Products quality comparable to virgin base oils (API Group II)	72	Residue used as asphalt extender or in bituminous membranes. Catalyst may be regenerated and re-used in the process.
1. Solvent extraction + hydrofinishing					
Snamprogetti	Acceptance of all used motor oil feedstock.	Relatively expensive due to 2 PDA units and hydrofinishing process	High-quality base oils.	74–80	Bottom fraction used in asphalt production. Losses of propane of about 5–10%.
Cyclon process	Acceptance of all used motor oil feedstock.	High operating and capital costs.	High-quality base oils.	72	Light hydrocarbon fuel-used as fuel in oil heaters on the plant or in boilers.

3.2. SOLVENT EXTRACTION

The process that transfer a solute from one liquid across a boundary of another liquid, partially miscible or immiscible is called solvent extraction (Blumberg 1988). This process is also described as the separation of a solute between two immiscible phases, generally liquid, that are in contact with each other (Rydberg 2004). Basically the separation of two immiscible or partially miscible phases is allowed by the introduction of a third substance, called extracting agent or extraction solvent. The solubility of the extracting solvent closely affects the distribution of the solute.

As mentioned above, considering this technique applied to the re-refining of waste oils, solvent extraction is the process that allows to separate reactive components, such as unsaturated hydrocarbons and other contaminants, from the lubricating oil, in order to improve the physicochemical properties of the oil. Basically the extraction technique can be applied using a single solvent or composite solvents. The presence of solvents may become the greenest process, reducing the production of acid sludge, the operating conditions such as lower temperature and pressure and the requirement of catalyst replacement (Daspit et al. 2000).

As stated by Alves Dos Reis and Jeronimo (1988) and Awaja and Dumitru (2006) the solvent must reject as much as possible the additives and all disperse particles from solution and be miscible with the base oil contained in the waste oil. At the same time it must also be stable, cheap and easy to recover. Moreover, the solvent selected for the extraction process should have low affinity with the undesirable compounds (Seader et al. 2011).

Several solvents have been studied and tested in the regeneration of waste lubricant. One of the most used is propane, because of its capability to precipitate contaminants such as heavy metals and asphaltenes and impurities as degraded additives from the waste oil phase (Andrews 1974) (Rincòn et al. 2003). The *Institut Francais du Petrole* (IFP) proposed a combined process between solvent extraction and acid/clay process (Vaughn 1975) using propane.

Disregarding the drawback of high risk of fire and explosion (Awaja and Dumitru 2006)) due to high pressure involved, supercritical propane has allowed to obtain good results of quality of the base oil, with yield of 72-80%. Similar solvents have been also used such as hexane and ethane (Rincón et al. 2007).

Burrell's classification is very important to choose the appropriate solvent (Burrell 1968), indicating that the solvents high removal capacity are alcohols such as butyl alcohol, methyl alcohol and 1-propanol, while the capacity of removal of impurities and contaminants of ketones is lower. This is due to the absence of hydrogen bond in ketones (Kamal and Khan 2009). Another important factor is the molecular weight of the extractant. If the solvent has a low molecular weight, corresponding to less than 3 carbons, it may not be able to dissolve base oils and solvents with chain with more than 5 carbons, hindering the flocculation of the impurities (Alves Dos Reis and Jeronimo 1988) (Rincòn et al. 2005).

The process of solvent extraction was studied for the removal of polymeric compounds and carbonaceous particles from the waste oil by (Alves Dos Reis and Jeronimo 1988) and (Martins 1997) using a mixture of alcohols and ketones in the presence of KOH. Potassium hydroxide promotes the flocculation of the impurities in alkaline conditions, which are then separated from the oil and the solvent. The hydroxyl group enhance the flocculation destabilizing the dispersion neutralizing the electrostatic repulsion, and consequently increase the sludge removal from waste oil (Mohammed et al. 2013).

Solvent extraction is a low energy consumption process when compared with hydrotreatment or vacuum distillation, which are much more energetically expensive, both technologies use high temperature, high pressure or deep vacuum. Indeed, due to economic advantages, solvent extraction is still subject of investigation to improve its characteristics (Fan 2010) (Lukic et al. 2006). It can be used as a deasphalting, finishing or even as a pretreatment step and it is usually combined with vacuum distillation, clay treatment or hydrotreatment (Kajdas 2014).

3.3. STATE OF THE ART

As mentioned before, the solvent extraction is not a new process, but it still under research in the field of regeneration of waste oils. Table 3.2 summarizes studies from the literature related to this subject, ordered by the year of publication.

In most of the works reported in Table 3.2, the experimental procedure adopted is the one described by Alves Dos Reis (1982), whereas in some cases little changes have been adopted. It is also evident that the most important factor that is taken into account in the solvent extraction process of waste lubricant oil is the solvent:oil ratio, followed by the mixing time, the dosage of flocculant, the extraction temperature and several others. Although many solvents have been tested, typically the most used are alcohols, ketones and light hydrocarbons. Table 3.2 shows that especially alcohols and ketones such as 1-butanol and MEK, respectively, are able to give the best performance in terms of extraction yield, sludge removal and oil loss. The works above confirm that the re-refining of waste lubricant oil by solvent extraction leads to a good quality base oil, involving mild operating conditions.

Table 3.2: Overview of studies from the literature related to solvent extraction.

Ref.	**Objective**	**Solvent**	**Operating condition**	**Main conclusions**
Martins 1997	Study the action of ternary solvent to re-refine lubricating oil, with solvent extraction process.	Mixture of n-hexane/ 2-propanol/ 1-butanol KOH (used as flocculant)	Initial distillation: T=160 °C; P=5 mmHg Solvent evaporation: T=150 °C; P=10 mmHg.	Optimal conditions at the composition of 0.25 waste oil, 0.35 n-hexane, and 0.40 polar compound (80% 2-propanol + 20% 1-butanol with 3 g/L KOH).
Nimir et al. 1997	Extraction process for recovering used lubricant oils using different solvents.	2-propanol 1-butanol methyl ethyl ketone	Extraction temperature: 25, 28, 50 °C. Solvent:oil ratio: 2:1-10:1	Alcohols produce the best sludge removal, while ketone achieves the minimum oil loss.
Rincòn et al. 2003	Regeneration of waste lubricant oil by propane extraction.	Liquid propane	Extraction temperature: 20-140 °C extraction pressure: 30-60kg/cm^2 extraction time: 0-5 hrs amount of oil: 25, 50, 75, 100 g	The pressure does not affect yield or contaminants removal. Optimal conditions are P = 30 kg/cm^2 and T = 90 °C.
Rincòn et al. 2005	Regeneration of used lubricant oil by polar solvent extraction. Effect of different solvent on the quality of re-refined oil.	2-propanol 2-butanol 2-pentanol methyl ethyl ketone methyl n-propyl ketone	Solvent:oil ratio: 1:1-15:1 mixing time: 5-60 min extraction temperature: 25, 40, 60 °C.	Increasing the solvent-oil ratio the yield is improved, up to a point at which it stabilizes. Increasing the solvent-oil ratio the quality of the oil recovered is improved, and this was observed with all solvents.
Lukic et al. 2006	Extraction process of waste insulating oil with N-methyl-2-pyrrolidone (NMP) via the three-stage mixer–settler operation.	N-methyl-2-pyrrolidone Water (used ad co-solvent)	Concentration of water: 0, 1, 3 (%, w/w) solvent:oil ratio: 0.5:1-1:1 extraction temperature: 40-90 °C	Moderate extraction temperature, 1% water in NMP and a low solvent/oil ratio (0.5) were determined to be the optimum process parameters.
Kamal and Khan 2009	Effect and performance on the sludge formation of different solvents used in the extraction process of waste lubricating oil.	n-heptane n-hexane methyl iso butyl ketone methyl ethyl ketone 1-butanol 2-butanol benzene 1-hexanol	Settling time: 0-50 hrs solvent:oil ratio: 2:1-6:1 extraction temperature: 15-60 °C	1-butanol and MEK achieve the best performance. Recovery of base oil with 94% yield.
Mohammed and Kheder 2009	Solvent extraction of waste lubricating oil to obtain lubricants with high viscosity index.	Furfural N-methyl-2-pyrrolidone	solvent:oil ratio: 1:1-4:1 extraction temperature: 70-110 °C	NMP is the best solvent, achieving a VI of 107.82 at 110°C and a solvent-oil ratio 4:1.
Ali et al. 2010	Purification of base oil by adsorption process, using zeolite for the removal of zinc and magnesium.	2-propanol methyl ethyl ketone (KOH as flocculant) (zeolite as adsorbent)	2^3 factorial design with: amount of zeolite 1-10 g temperature 30- 70°C contact time 5 -60 min.	The removal of zinc is better than the one of magnesium. The most affecting variable is the time of adsorption
Durrani et al. 2012	Determining an efficient solvent extraction parameters for re-refining of waste lubricating oils	1-butanol 2-propanol methyl ethyl ketone	solvent:oil ratio: 1:1-7:1 extraction temperature: 20, 30, 50 °C	Methyl ethyl ketone achieved the highest sludge removal and the lowest oil loss.
Katiyar and Husain 2012	Re-refining process of used lubricating oil by solvent extraction.	1-butanol 2-propanol methyl ethyl ketone methyl iso butyl ketone	Solvent:oil ratio: 1:1-11:1 Extraction temperature: 20, 30, 40, 48, 50, 52 °C.	The maximum sludge removal was produced by 1-butanol, while the minimum percentage of oil loss was achieved by 2-propanol.

Table 3.2: Overview of studies from the literature related to solvent extraction (continued).

Ref.	Objective	Solvent	Operating condition	Main conclusions
Emam and Shoaib 2013	Re-refining of used lubricant oil by solvent extraction and vacuum distillation followed by hydrotreating.	methyl ethyl ketone	Solvent:oil ratio: 3:1-7:1 settling time: 24-48 hrs vacuum distillation performed at 310 °C and 15mmHg.	The best results were obtained by a solvent to oil ratio of 5:1 at 24 hrs settling time. Higher yield (84%) using vacuum distillation, with respect to extraction yield (78%).
Mohammed et al. 2013	Recovery of base oils from waste lubricant using a novel combination of solvent extraction and adsorption on solids.	n-hexane 1-butanol 1-hexanol carbon tetrachloride petroleum ether acetone KOH (used as flocculant)	Solvent :oil ratio: 1:1 - 4:1 KOH dosage: 1-3 g/L	1-butanol achieved the best performance for PSR followed by n-hexane, petroleum ether, 1-hexanol, carbon tetrachloride, and acetone.
Yang et al. 2013	Identify the best refining conditions to separate base oil from waste oil.	i-butanol n-butanol MEA (used as flocculant)	Solvent:oil ratio: 1:1-11:1 MEA concentration: 1-3 g/kg mixing time: 5-50 min extraction temperature: 10-50 °C	Optimal conditions are mixing time 20 min, extraction temperature 30 °C, MEA concentration 2g/kg, solvent:oil ratio 5:1. Higher extraction yield obtained for the solvent i-butanol/MEA
Hussein et al. 2014	Investigate the re-refining of used lubricating oils using solvent extraction process.	butyl alcohol 1-propanol acetone	Mixing time: 5, 15, 25 min mixing speed: 400, 800, 1200 rpm extraction temperature: 25, 40, 60 °C.	Extraction with butyl alcohol gives the highest yield of 93.4%, followed by 1-propanol (90.7%), lower value for acetone (51%).
Kamal et al. 2014	Optimize the liquid-liquid extractive re-refining of waste lubricants.	methyl ethyl ketone 1-butanol	Settling time: 10-50 hrs extraction temperature: 10-60 °C solvent:oil ratio: 2:1-6:1	Alcohol is superior over ketone, it shows a better removal of PAH and superior sludge removal (>8%).
Omolara et al. 2015	Regeneration of waste lubricant engine oil by solvent extraction process, comparing the performance of different solvents.	1-butanol 2-propanol mixtures of 1-butanol-ethanol	Solvent:oil ratio: 1:1-6:1 mixing time: 20, 30 min extraction temperature: 35, 45, 50°C.	Mixing time does not highly affect the PSR, instead solvent-oil ratio does it. Best results achieved with 1-butanol with SOR of 3:1.

PSR- Percentage of sludge removal

4. MATERIALS AND METHODS

In this section will be described the procedures used in the extraction process of waste lubricant oils, as well as the analytical techniques and the materials used in the experiments.

4.1. MATERIALS

The waste lubricant oil pretreated (about 10 L) was provided by SOGILUB. The solvents tested are listed in the Table 4.1. In addition, KOH hydroxide in pellets of AzkoNobel Eka (MW 56.11 g/mol) was also used in the extraction experiments.

Table 4.1: List of solvent used.

Solvent	Formula	Properties	Supplier/purity
1-Butanol	$CH_3(CH_2)_3OH$	MW= 74,12 g/mol, bp = 116-119 °C	Carlo Erba/ ≥ 99.5%
MEK	$CH_3COC_2H_5$	MW= 72,11 g/mol, bp = 80°C	Sigma-Aldrich/ ≥ 99.5%
N-Hexane	$CH_3(CH_2)_4CH_3$	MW = 86,18 g/mol, bp = 69 °C	LabChem/ ≥ 99.5%
Isopropanol	$CH_3CH(OH)CH_3$	MW = 60,10 g/mol, bp = 82°C	Sigma-Aldrich/ ≥ 99.8%

4.2. EXTRACTION PROCEDURE

The experimental extraction procedure was performed according to the study done by Alves Dos Reis (1982), Nimir et al. (1997) and Karim (2004)

Previously weighed centrifugal tubes are filled with a mixture of 20 g of used oil sample (W_{oil}) and solvent ($W_{sol.}$) at a pre-specified ratio. The samples are then stirred in a plates (OVAN) at specified time and 500 rpm, using PTFE magnets-stirring bar to ensure adequate mixing and avoid loss of oil on the wall of the tubes. The temperature is kept constant at 25°C by the stirring plates. The tubes are introduced in the centrifuge (Nahita model 2655), at 4000 rpm for 10 min. Then, the wet sludge phase (additive, impurities and carbonaceous particles) is separated from the mixture solvent/oil.

The solvent is recovered from the solvent/oil mixture by vacuum distillation, using a STUART vacuum pump RE3022C, in a rotary evaporator with a STUART oil bath RE3000B. The temperature of the oil bath is set considering the boiling point of the solvents. The distillation flasks are previously weighted, and the mass of the recovered oil and solvent can be calculated by difference.

The extraction yield is calculated by Eq (4.1), as the mass of recovered oil, $W_{\text{base oil}}$, expressed in grams, separated from the initial waste oil, $W_{\text{used oil}}$.

$$Yield\ (\%) = \frac{W_{base\ oil}}{W_{used\ oil}} \times 100 \tag{4.1}$$

The tubes with the wet sludge are introduced into an oven (CARBOLITE), at 105°C for 90 min in order to evaporate the solvent that is trapped in the wall of the falcon. The wet sludge is washed using 7 mL of n-hexane and 28 mL of isopropanol to separate the sludge. The addition of isopropanol immediately produces large flakes. The washing process is anticipated to remove about 95% of interstitial oil content present in the sludge phase.

Finally, the washing liquid is discarded, and the tubes are introduced into an oven in which the sludge is dried for 1 hour at 105ºC. After cooling in a desiccator, the tubes are weighed and the percent sludge removal, PSR, and the percentage oil loss, POL, are calculated by Eq (4.2) and (4.3).

$$PSR\ (\%) = \frac{W_{dry\ sludge}}{W_{used\ oil}} \times 100 \tag{4.2}$$

$$POL\ (\%) = \frac{W_{wet\ sludge} - W_{dry\ sludge}}{W_{used\ oil}} \times 100 \tag{4.3}$$

4.2.1. Viscosity and Viscosity Index

The viscosity was measured using a Tamson TV 2000 bath with Cannon-Fenske opaque viscometers, according to ASTM D445. A viscometers from series 200 and 300 were used, in order to have an adequate flow time. The kinematic viscosity is calculated by Eq. (4.4)

$$\text{Kinematic Viscosity} = \mathrm{C} \times \mathrm{t}\ [\mathrm{cSt}] \text{ or } [\mathrm{mm}^2/\mathrm{s}] \tag{4.4}$$

where C (mm^2/s^2) is the intrinsic constant of the viscometer capillary tube and t (s) is the flux time that samples takes to flow freely from the lower to the upper meniscus mark of the viscometer. Viscosity was determined at 40°C and 100°C, and then the viscosity index (VI) was calculated according to ASTM D2270.

4.2.2. Total Acid Number

Total Acid Number (TAN) is determined according to ASTM D664, based on potentiometric titration, using the volumetric titrator Metrohm 905 Titrando. The potential is measured by the Solvotrode EasyClean electrode, with an electrolyte solution of lithium chloride saturated with ethanol. The mass of the samples depends on the expected TAN, and is mixed with a solvent composed by toluene, isopropanol and water (50, 49.5 and 0.5% v/v, respectively). The titration is performed with isopropanol potassium hydroxide solution (0.1 M). Before the measurement, is required to perform a blank, doing the determination without the sample and using only the solvent.

TAN corresponds to the weight (milligrams) of KOH required to neutralize one gram of the constituents of the oil that react with KOH, as indicated by Eq (4.5):

$$\mathrm{TAN} = \frac{(\mathrm{V_s} - \mathrm{V_{blank}})\, \mathrm{C_{KOH}}\, \mathrm{f}\, \mathrm{M_A}}{\mathrm{m_s}} \ [\mathrm{mg\ KOH/g}] \tag{4.5}$$

where V_s (mL) is the volume of titrant spent until the equivalence point, V_{blank} (mL) is the volume of titrant spent to the equivalence point when determining the blank, C_{KOH} is the concentration of the titrant (0.1 M), f is the correction factor for the concentration of titrant, M_A is the molar mass of KOH (56.106 g/mol) and m_s (g) is the sample mass weighted.

4.2.3. Elemental Analysis

The measurement of the concentration of metals and other elements such as sulfur and chlorine, was performed by Energy Dispersive X-Ray Fluorescence (EDXRF), using Nex CG Rigaku spectrometer. In this technique, the sample is excited by a source of X-Rays and the emission of X-Rays by the atoms will be unique, since each chemical element differs from the others under the atomic structure point of view, this allows the characterization of the sample. The electrons in an electron layer inside the atom are excited by the incident beam, provoking their ejection. When they return to the voids previously created a specific amount of energy is emitted as X-ray. The EDXRF measures the energy and number of the X-Rays emitted by atoms.

The equipment used allows the analysis of element from sodium (^{11}Na) to uranium (^{92}U). In order to increase the accuracy of the equipment, the organic matrix effect must be subtracted.

4.2.4. FTIR

For the detection of functional groups present in used and regenerated lubricating oils Fourier Transform Infrared Spectroscopy (FTIR) was used. The analyses were conducted in a spectrophotometer Jasco FT/IR–4200 (CIEPQPF Research Center), within the range 4000-500 cm^{-1} using 64 scans/sample at 4 cm^{-1} resolution. Measurements were performed in KBr pellets that are prepared using a pneumatic press. Before scanning each sample, the background spectrum of the KBr pellet without the sample must be taken and subtracted. A drop of lubricating oil sample was placed on the surface of the KBr pellet, creating a thin film.

4.3. SURFACE RESPONSE METHODOLOGY

To investigate the influence of three factors (solvent-oil ratio, mixing time and KOH dosage) in yields, PSR and POL a full factorial design was implemented. The main objective was optimizing the experimental conditions in the solvent extraction process.

The data obtained from the full factorial design was analyzed using the response surface methodology (RSM), which is useful for developing, improving, and optimizing processes (Myers et al. 2008). The RSM takes the data obtained experimentally, and by regression analysis provides functions that can be graphed as surface (Agbaba et al. 2016).

The software used to implement the design of experiments was JMP Pro version 12.1.0.

The design of experiment chosen was the full factorial design, it contains all possible combination of a set of factors. The full factorial is the most complete design approach, but it is also the most costly in experimental resources.

5. RESULTS AND DISCUSSION

The experimental methodology of this research was conducted as described in the previous chapter, and the results will be presented and discussed in five different sections. The first section describes the selection of the two solvents. The second part reports the choice of the process variables, explaining the reasons of the variable adopted, according to the literature, and highlighting their importance on the solvent extraction process. The third and the fourth sections present the solvent extraction studies with MEK and 1-butanol, respectively. Finally in the fifth section, a comparison between the two solvents is pointed out, indicating the best performance obtained between them.

5.1. SELECTION OF THE SOLVENTS

The solvent that is selected must achieve two important characteristics: it has to be miscible with the base oil contained in the used lubricant and should reject from the solution the additives and the dispersed particles allowing their aggregation in particles with enough diameter to be separated by sedimentation or other similar method (e.g. centrifugation).

In previous works Alves Dos Reis and Jeronimo (1988); Rincòn et al. (2003,2005,2007) and Mo et al. (2007) several organic solvent, such as alcohols, ketones and hydrocarbons were applied to treat waste oil, because they achieve the constraints above mentioned.

According to Yang et al. (2013), the main points considered in the selection of the optimal extractant are the Hildebrand solubility theory of the solvents, the selectivity of the solvent for extracting base oil from waste oil, and the existing background on the regeneration process of used oil by solvent extraction. Furthermore, it was also considered several criteria of the selection guide for solvents (ACS GCIPR 2011 and ESI 2010) in terms of green chemistry and sustainability (Henderson et al. 2011).

First of all, Hildebrand solubility theory states that the particles and impurities of high molecular weight present in the waste oil can be dissolved more easily by the heavier solvents, because of their similar solubility parameter (Hildebrand and Scott 1964). Accordingly, in this work low molecular weight solvents were used, in order to avoid the dissolution of impurities particles in the liquid phase. Considering the studies reported by Rincòn et al. (2005) and Alves Dos Reis and Jeronimo (1988), ketones and the alcohols containing three to five carbon atoms, were used to regenerate waste oil; while liquid hydrocarbons are not recommended because their ability to extract also macromolecular compounds and other additives. Their studies suggest that the alcohols will lead to better dissolution of impurities then ketones.

The selection of solvents in this study took into account three indicators: the efficiency results reported in the literature; the “greenness” of solvents regarding factors such as the environmental impact; and low price. The alcohol and ketone solvent that better met the requirements stated above were selected. Therefore, methyl ethyl ketone (MEK) and 1-butanol are the solvents studied in this work.

5.2. SELECTION OF THE VARIABLES

In the literature, several variables were identified with high influence on the regeneration of waste oil by solvent extraction. In this work, the variables selected to analyze the process performance were the solvent to oil ratio (SOR), the dosage of KOH and the mixing time. Other variables that could be analyzed are the settling time (Kamal and Khan 2009), the extraction temperature (Durrani et al. 2012), the extraction pressure (Rincòn et al. 2003), the stirring speed (Hussein et al. 2014) etc.

The SOR plays a fundamental role in the extraction process, because establishes the amount of base oil that can be dissolved. In general, the higher the amount of solvent leads to higher amount of oil that can be recovered. The effect of KOH is to promote and speed up the flocculation of impurities in order to allow the solvent to segregate them from the base oil.

The tests performed by Alves Dos Reis and Jeronimo (1988) on waste oil demonstrated that the carbonaceous compounds remain in a stable dispersion. They stated that this behavior is explained by the polar nature of the solvent (alcohol), and suggested the introduction of KOH to break the stability by neutralizing the exceeding charges in the solution. The stability of particles in suspension is controlled by the chemical and electrical parameters of the system. The flocculation of charged particles can occur by two mechanisms: reduction of the electrostatic repulsion between particles and formation of bridges between particles. By mixing KOH with the organic solvent, the carbonaceous or similar particles follow the first mechanism.

The effect of mixing time is important because it is the time in which the solvent, flocculant and waste oil are in contact. This time should be long enough to allow the solvent to act on the base oil contained in the waste one. Furthermore, it should allow flocculant to neutralize charges of impurities in order to break stabilization by electric repulsion (Martins 1997).

5.3. EXTRACTION WITH MEK

The extraction process was performed according to the procedure described in section 4.2. To determine the optimal conditions of the extraction, a full factorial design with three levels was implemented. Thus, 27 experiments were performed randomly in order to avoid any potential bias or judgments.

In Table 5.1 the levels of the process variables are shown, whose assignment of values were based on studies reported in the literature. The results are reported in Appendix.

Table 5.1: Process variables and levels tested.

Process Variables	**Level**		
	Low(-)	**Medium(0)**	**High(+)**
Solvent/oil ratio	1	3	5
KOH dosage (g/L)	1	2	3
Mixing time (min)	10	20	30

As previously referred, the main goal of the work is to optimize the extraction conditions. In this context, JMP statistical software was used to find optimal based on the full factorial design results. JMP has special features in multiple-response models to help judge the conditions that optimize a complex set of criteria.

Figure 5.1 show the predicted profile developed from the full factorial design results and the optimal conditions. The prediction trace (black line) show how the predicted response value changes for each factor. The 95% confidence interval for the predicted values is shown by a dotted blue curve surrounding the prediction trace. For each response, a desirability function (right column) was determined, that allows to find optimal settings for all the responses simultaneously. The maximum desirability must correspond to a tradeoff between the maximum values of Yield and PSR and at the same time a minimum POL. The bottom row of Figure 5.1 shows the desirability trace for each factor. The overall desirability can be defined as the geometric mean of the desirability for each response on a scale of zero to one. Finally, the red dotted lines (vertical and horizontal) shows the optimal value of each factor and correspondent response that maximizes the desirability. The results show that optimal conditions are obtained for a SOR of 2.5, a KOH dosage of 1.6 g/L and a mixing time of about 14 min, that achieves a maximum Yield of 92.3%, a PSR of 6.7% and a minimum POL of 6.1%.

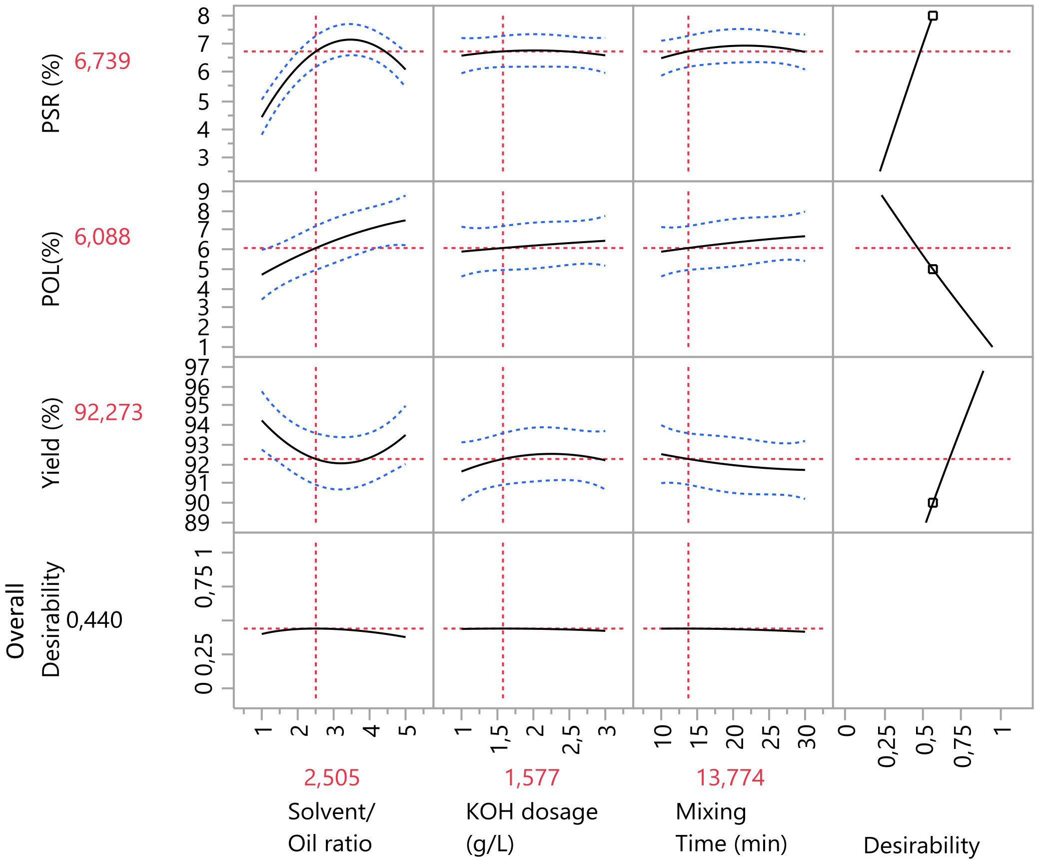


Figure 5.1: Optimized results for MEK.

The data obtained from the full factorial design has been analyzed using the response surface methodology. Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes (Myers et al. 2008). The RSM takes the data obtained experimentally, and by regression analysis provides functions that can be graphed as surface (Bezerra et al. 2008).

To obtain a regression equation the different response functions were generated and correlated with the experimental data. It was chosen the quadratic model, that guarantees the best fit of experimental data with the lowest standard deviation. The responses were modeled as a second-order polynomial equation, Eq (5.1):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1 \leq i \leq j}^{k} \beta_{ij} x_i x_j + \varepsilon \qquad (5.1)$$

where Y is the predicted response (Yield, PSR and POL), k is the number of factors (#3), x_i represents the different factors (SOR, KOH dosage and mixing time); β_0 is the constant coefficient and $\beta_i, \beta_{ii},\ \beta_{ij}$ are the coefficient of the linear, quadratic and interaction terms, respectively.

The second order polynomial functions obtained for the three responses are:

$$Yield(\%) = 97.9420 - 3.77289A + 0.45302A^2 + 1.61816B - 0.58109B^2 - 0.23720C + 0.00156C^2 + 0.24029AB + 0.03551AC + 0.02860BC \tag{5.2}$$

$$PSR\ (\%) = 9.21047 + 1.49072A - 0.36933A^2 - 2.74820B + 0.14173B^2 - 0.16706C - 0.00002C^2 + 0.32136AB + 0.01634AC + 0.04631BC \tag{5.3}$$

$$POL\ (\%) = 0.30055 + 1.711902A - 0.085623A^2 + 1.284579B - 0.03086B^2 + 0.15682C - 0.00069C^2 - 0.179067AB - 0.015833AC - 0.03161BC \tag{5.4}$$

where A, B and C are solvent-oil ratio, KOH dosage and mixing time, respectively. The values of the coefficient of determination,R^2, are presented in Table 5.2.

Table 5.2: Coefficients of determination for the responses using MEK as solvent

Response	$\boldsymbol{R^2}$
Yield	0,534
PSR	0,741
POL	0,499

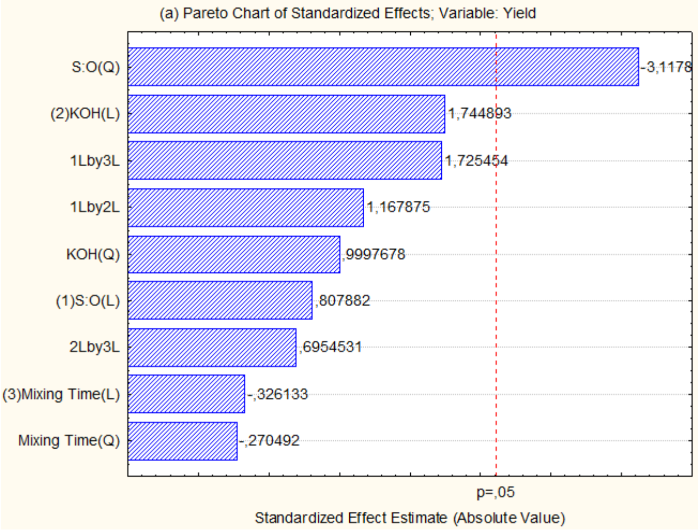
Considering the low magnitude of R^2, it is evident that the model responses do not fit quite well with the experimental data. Indeed, the best results was obtained for PSR , with a coefficient of determination of 0.741, which means that only about 74% of the variation of PSR is explained by the variations of the A, B and C factors. Indeed, some measurements are subject to some uncertainty due to critical issues that were faced during the execution of the experimental tests. For example, for low SOR values it was really hard to achieve a complete separation between the sludge and the mixture (solvent + base oil). Even increasing the speed of the centrifuge and its time, sometimes the two phases were not well separated. This problem was studied by Alves Dos Reis (1982), that identified a critical SOR, at which the removal of contaminants cannot occur. It is important to note that the critical ratio (CR) value depends on the temperature. For MEK, the CR has been reported as 0.9, 1.15 and 1.40 at 20, 35 and 50 °C, respectively. As stated before, the experiments in the present study were performed at 25 ± 2°C, and little differences in the temperature can lead to a difficult phase separation, where the sludge phase is not well sedimented and remains mixed with the liquid phase.

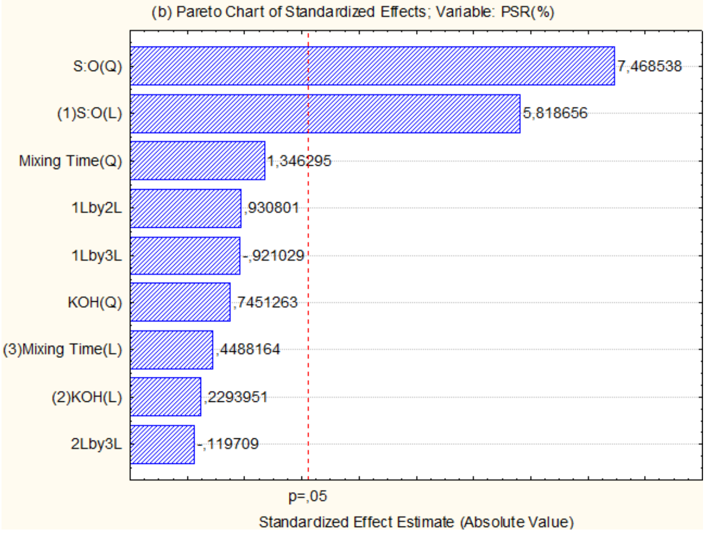
The importance of the three factors on the response variables was carried out using the STATISTICA software. For that purpose, a Pareto chart is useful to identify the most and less important factors that influence the treatment performance by solvent extraction. Figure 5.2 shows effect of linear, quadratic and interaction terms on the three responses. These results suggest that the solvent to oil ratio is the most relevant factor for the yield, PSR and POL. In addition, it can also be seen that the mixing time is the less significant term, affecting in a negligible way the responses. These Pareto charts are obtained from the experimental results of the full factorial design, which leads to the optimal conditions reported in Figure 5.1. Considering this, the models reported in Eq. (5.2) to (5.4) may be simplified, since the effect of the SOR should be considered the most relevant.

Considering the difficulties in extracting reliable conclusions from these results, it was decided to carry out another set of tests. These tests aim to figure out the general behavior of the three responses by varying the most significant process variable in a wide range, in order to define consequently the optimal range to be adopted in the experimental design.

Figure 5.3 shows the importance of the SOR in a range from 1 to 12. As expected, the Yield increases with increasing SOR (Figure 5.3 (a)) up to a ratio of 6:1. According to studies reported in the literature (Rincòn et al. 2005; Yang et al. 2013) this behavior can be explained by the combined effect of the following factors: at lower ratios, the solvent is not able to dissolve all the base oil that is contained in the waste oil; increasing SOR the amount of base oil that can be dissolved increase, up to a point at which all the base oil is dissolved.

From Figure 5.3 (b) it can be observed that increasing the solvent-oil ratio the PSR increases until around 6% (maximum value) and then decreases. On the contrary, the POL seems to increase continuously when SOR increases.





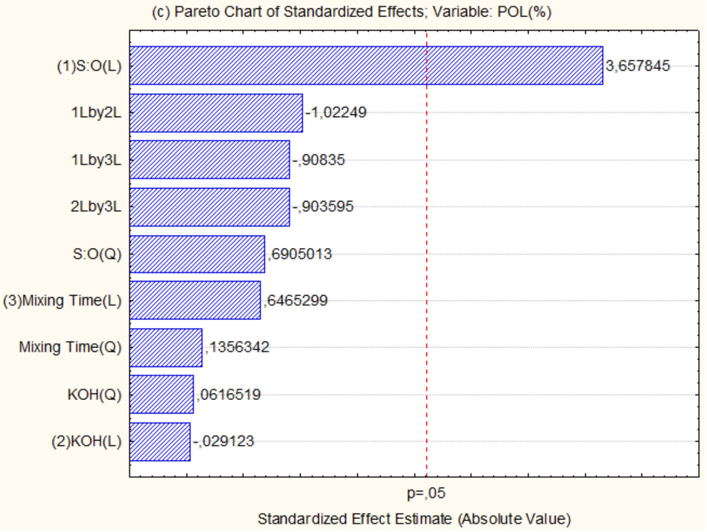


Figure 5.2: Pareto Chart of standardized effects for (a) Yield, (b)PSR and (c) POL.

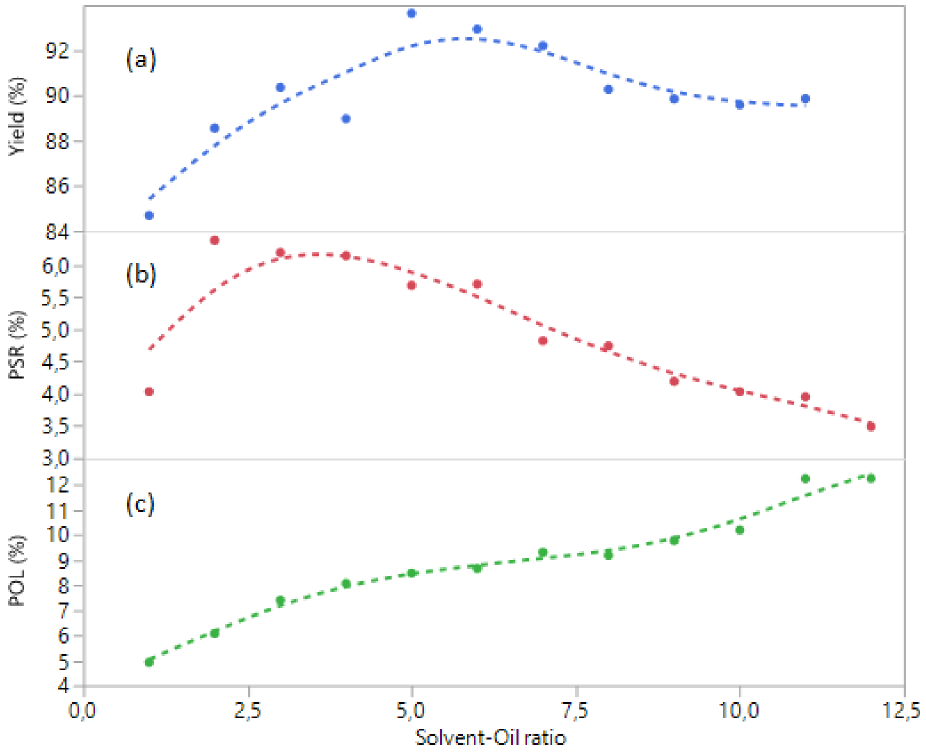


Figure 5.3: Behavior of (a) yield, (b) sludge removal, (c) oil loss as a function of SOR.

The trends observed for PSR and POL were not expected taking into account what was previously found in the literature. Indeed, Elbashir et al. (2002) stated that the percent of oil losses was found to decrease as SOR increases. This phenomenon can be explained considering that if the SOR rises, is also enhanced the mutual solubility of oil in the solvent, resulting in a sludge phase with lower content of oil. Mohammed et al. (2013) also indicated that an increase in SOR leads to higher sludge removal, up to a point at which a maximum value is achieved. This is explained again based on the medium mutual solubility of oil in the solvent.

To overcome these experimental problems and improve the quality of the results different strategies were applied. It was decided to repeat some tests, applying some modifications in the experimental procedure and in the experimental design.

In order to achieve reliable results for the Yield, the temperature of the bath during the vacuum evaporation was increased, in order to ensure the complete removal of solvent from the base oil. The temperature was settled at 162 °C, much more higher than the boiling point of the solvent, even taking into account the role played by the vacuum pump. The presence of solvent into the re-refined oil may affect the values of the Yield especially for higher SOR, where the amount of oil is very low.

Another modification was applied after the centrifugation and before the measurement of the wet sludge. It was noticed that inside the falcon, after the removal of the liquid phase destined to the rotary evaporator, the walls of the tubes were still wet. The percentage of oil loss is calculated using the data of the wet sludge, but this measurement is compromised by the presence of residual solvent inside the falcon. To overcome this problem, as reported in section 4.2, the falcon tubes were left for 90 minutes in the oven at 105°C, to evaporate the residual solvent attached to the wall and to the sludge.

Considering the Pareto charts reported above, it was decided change the experimental design, neglecting the mixing time and considering only SOR and KOH dosage. As reported in Table 5.3 the range of process variables was changed, in order to overcome the lowest critical ratio and be sure that the separation performed with the centrifuge was enough to separate the sludge phase and the liquid phase.

Table 5.3: Process variables and their levels

Process Variables	**Level**		
	Low(-)	**Medium(0)**	**High(+)**
Solvent/oil ratio	2	4	6
KOH dosage (g/L)	0	2	4

Response surface designs are useful for modeling a curved quadratic surface to continuous factors. A response surface model can find minimum or maximum response, if one exists inside the factor region. The most popular response surface design is the central composite design (CCD), it combines a two-level fractional factorial and two other kinds of points: central points and axial points. In central points all the factor values are at the zero.

A central composite design (CCD) with two central points was now adopted to analyze the treatment system, because of the low number of run (10) that it expects. The obtained results are indicated in Table 5.4.

Table 5.4: Operating conditions and the results obtainedwith MEK using a CCD.

N° Test	Mass oil (g)	Mass solvent (g)	Regenerated oil (g)	Yield (%)	PSR (%)	POL (%)
1	6.69	13.34	6.10	91.26	4.08	0.96
2	6.69	13.33	5.92	88.56	5.50	1.11
3	6.68	13.33	6.00	89.86	5.62	0.76
4	4.01	16.01	3.68	91.72	4.24	0.75
5	4.03	16.11	3.63	89.91	4.17	0.87
6	4.18	16.04	3.75	89.69	5.45	0.91
7	4.02	16.03	3.66	91.00	5.77	0.89
8	2.91	17.21	2.69	92.34	3.02	0.79
9	2.86	17.14	2.58	90.41	5.46	0.73
10	2.87	17.14	2.63	91.64	5.40	0.70

In Figure 5.4 can be seen the pattern of the Yield for three different concentration of flocculant (KOH). It is important to notice that in the case of the KOH dosage is 2 or 4 g/L, the Yield increases with increasing solvent-waste oil ratio, up to a point at which it stabilize. As mentioned above, this is due to the fact that at the lower ratio the solvent is not enough to dissolve all the base oil, while then the base oil is completely dissolved and the yield stabilize (Rincòn et al. (2005) and Yang et al. (2013)).

These results are in accordance with (Yang et al. 2013), that stated that the stabilization without any flocculant agent occurs at higher ratios than when KOH is used. Therefore, it can be concluded that the KOH could not only agglomerate used oil impurities, but also reduce the amount of solvent to accelerate stabilization of the response.

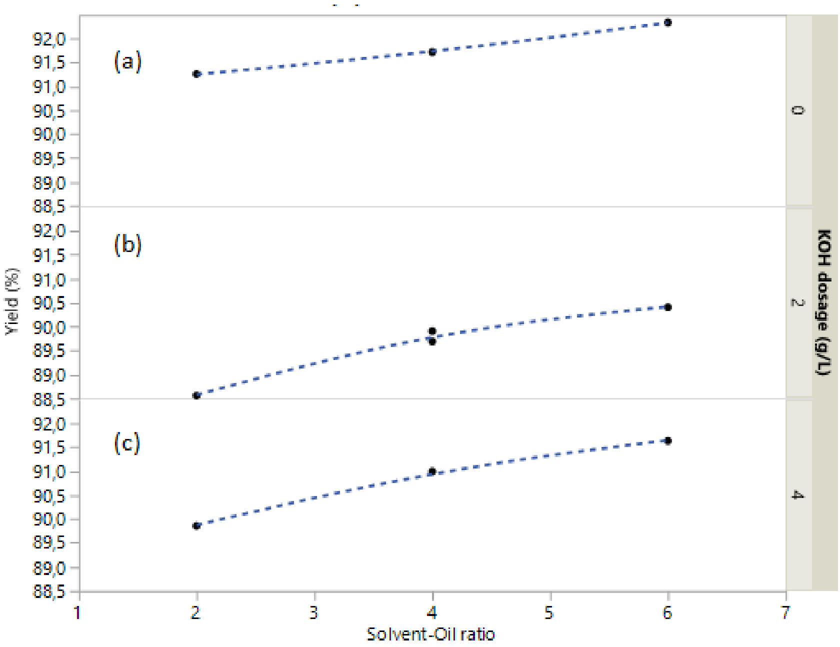


Figure 5.4: Effect of the solvent-oil ratio on the yield with 0 g/L of KOH (a), 2g/L of KOH (b) and 4g/L of KOH (c)

It can also be seen in Figure 5.4 that the Yield of the recovered oil is higher in the case of none KOH is used than with the mixture solvent and flocculant. A possible explanation for this behavior is that without KOH, impurities and contaminants did not completely agglomerate and a portion of them is coextracted with the base oil.

Even changing the experimental design and the levels of the process variables the sludge removal never assumed the expected pattern, which means that the removal of contaminants should increase as the SOR increases (Nimir et al. 1997). Indeed, the performed experimental tests never led to those results, and the data obtained always replicates the behavior shown in Figure 5.3 (b). Although several strategies were adopted in order to find out the reasons of this pattern, the solution is still unknown. Thus, more research is needed to explain the effect of solvent to oil ratio on the sludge removal.

Finally, the effect of SOR on the percentage of oil loss at different concentration levels of KOH was examined, and the results are showed in Figure 5.5.

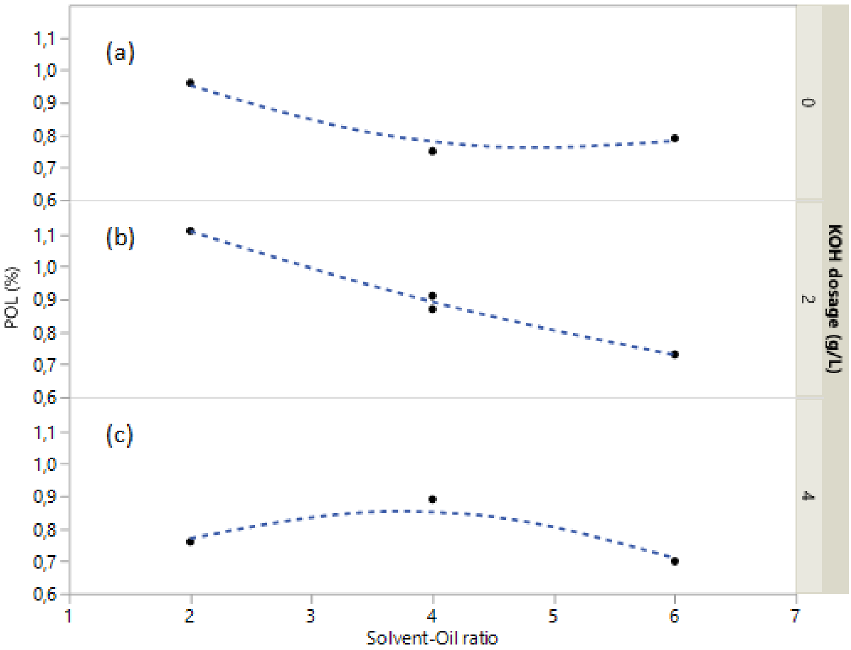


Figure 5.5: Effect of the solvent-oil ratio on POL with 0 g/L of KOH (a), 2g/L of KOH (b) and 4g/L of KOH (c)

In Figure 5.5 in (a) and (b) can be clearly observed a decrease in the oil loss, when the amount of solvent rises. Figure 5.5 (c) shows a different trend, especially for low ratios (2:1). As mentioned above, this can be explained considering that the mutual solubility of the oil in the solvent is enhanced when the SOR increases, and because of that the sludge phase trapped a lower quantity of oil.

Regression analysis was performed on the data thus obtained, using the STATISTICA software. The Equations (5.5) and (5.6) report the regression coefficient for Yield and POL.

$$Yield(\%) = 89.94143 + 0.67214A - 0.004589A^2 - 2.10143B + 0.42286B^2 + 0.04375AB \tag{5.5}$$

$$POL(\%) = 1.10119 - 0.070298A + 0.00071A^2 + 0.057143B - 0.024286B^2 + 0.00688AB \tag{5.6}$$

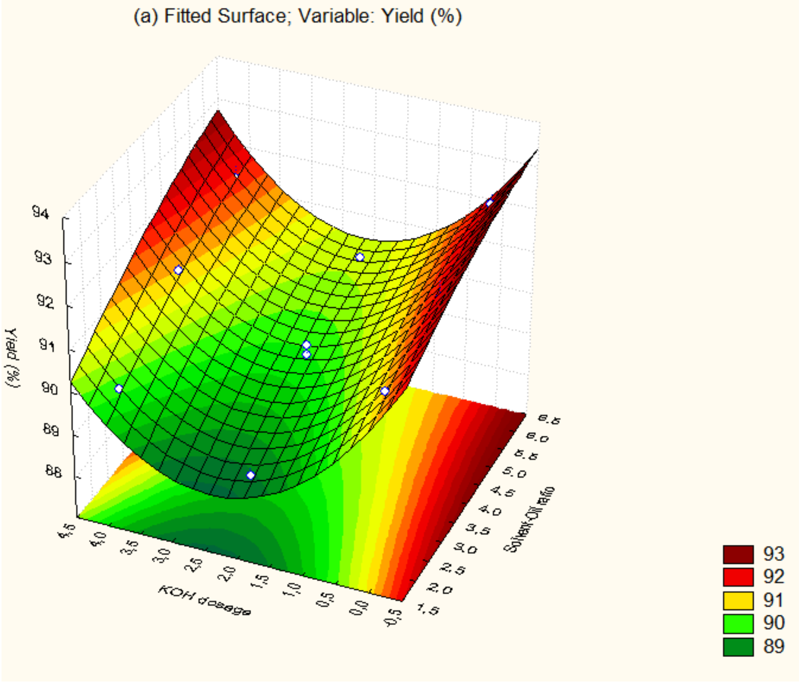
The statistical significance of the models was evaluated using the R^2 values, which are reported in Table 5.5. The results show that the model can fit quite well the experimental data, especially for the Yield. Both values are improved compared with the results of Table 5.2.

Table 5.5: Values of $\boldsymbol{R^2}$ for the responses

Response	$\boldsymbol{R^2}$
Yield	0.987
POL	0.634

The simultaneous effect of process variables upon Yield and POL during extraction with MEK can be seen in response surface depicted in Figure 5.6.

Figure 5.6 a-b give a good indication of the optimal conditions for the extraction process. In Figure 5.6 (a) can be noticed that the Yield is maximized for the upper value of the SOR and the external values of the considered range KOH dosage. In Figure 5.6 (b) the POL reaches the optimal conditions (minimized) for the same values of SOR and KOH dosage. For what stated above, it is reasonable to assume that the quality of the base oil will be improved with an higher concentration of flocculant agent. Thus, it is desirable to use a solvent with 4 g/L of KOH to achieve optimal conditions.


(a) Fitted Surface; Variable: Yield (%)

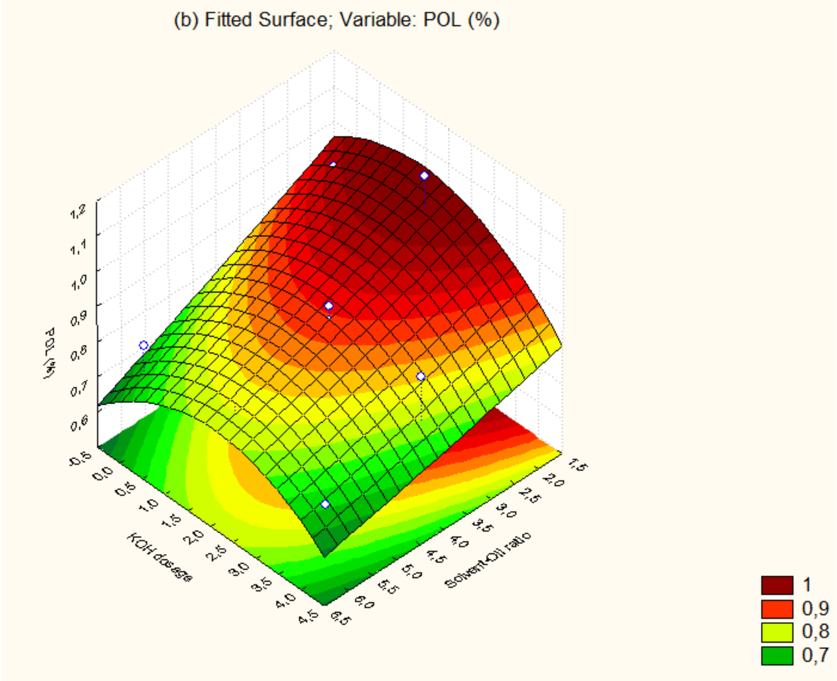

(b) Fitted Surface; Variable: POL (%)

Figure 5.6: Response surface, (a) yield, (b)POL.

5.4. EXTRACTION WITH 1-BUTANOL

The extraction process with 1-butanol was performed according to procedure described in section 4.2. A full factorial design with three levels was selected to figure out the optimal extraction conditions. The levels of the factors (process variables) are the same adopted for MEK (see Table 5.1). As already mentioned before, the optimal conditions require to find values of the process variables that allow the maximization of the Yield and PSR and minimize the POL. A first screening of the results was performed using the software JMP to maximize the desirability.

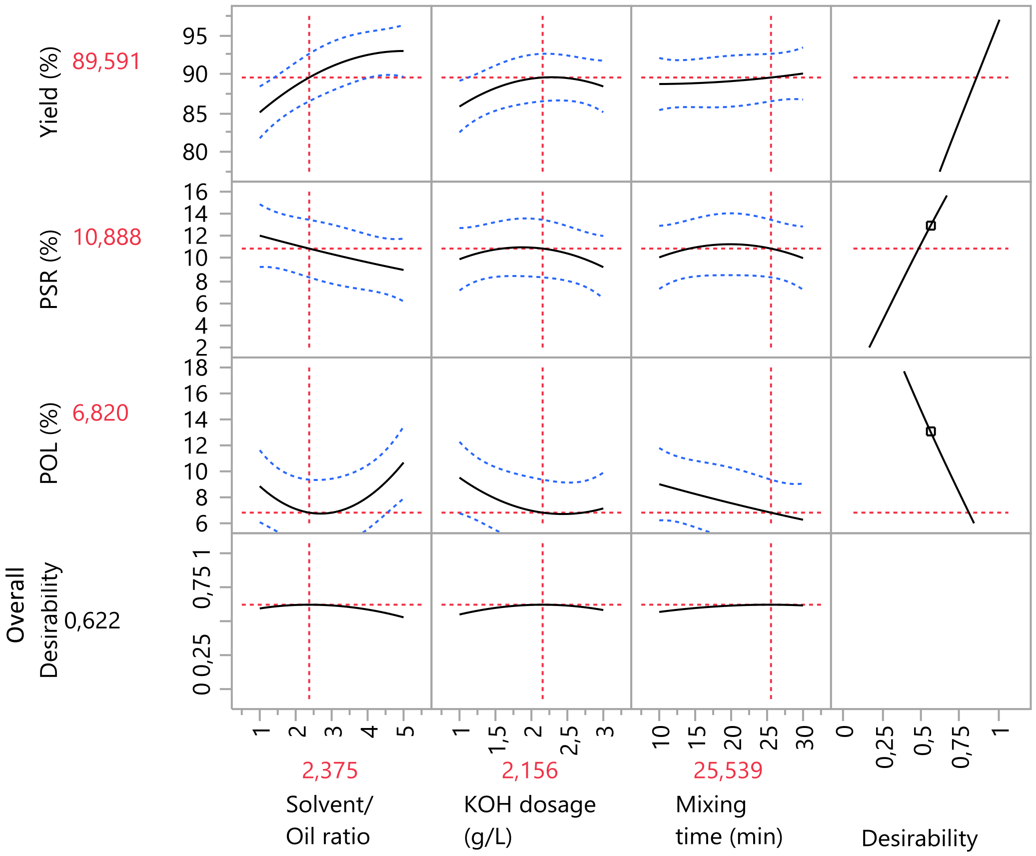


Figure 5.7: Optimized results for 1-butanol.

Figure 5.7 shows that the values that maximize the desirability are slightly increased compared with the ones obtained for MEK, and while the yield is lower, the PSR is better than depicted in Figure 5.1. This first screening of the results seems to confirm the reported in the literature, which is alcohols are better solvents in term of removal of contaminants.

The regression models for modeling the responses were based on second-order polynomial equations:

$$\begin{aligned} Yield(\%) = {} & 59.85407 + 6.13583A - 0.48972A^2 + 13.58306B - 2.29056B^2 \\ & + 0.22143C + 0.00304C^2 - 0.25583AB - 0.02646AC - 0.09875BC \end{aligned} \tag{5.7}$$

$$PSR(\%) = 4.37296 - 1.45806A + 0.02861A^2 + 4.73819B - 1.40556B^2 + 0.52564C - 0.01214C^2 + 0.33875AB - 0.00842AC - 0.01083BC \tag{5.8}$$

$$POL(\%) = 29.12954 - 6.02278A + 0.73806A^2 - 7.36792B + 1.35889B^2 - 0.330267C + 0.00091C^2 + 0.24042AB - 0.05996AC - 0.00683BC \tag{5.9}$$

where A, B and C are solvent-oil ratio, KOH dosage and mixing time, respectively.

The coefficients of determination R^2 are presented in Table 5.6. This can be justified by uncertainty in some results due to the same problems faced with the tests performed with MEK, namely difficulties in the separation of the sludge phase for low solvent to oil ratios.

Table 5.6: Coefficient of determination for the responses using 1-butanol as solvent

Response	$\boldsymbol{R^2}$
Yield	0,733
PSR	0,366
POL	0,510

Pareto charts were also obtained for this solvent, in order to verify the importance of the process variables. As can be observed in Figure 5.8, it is possible to analyze the effect of linear, quadratic and interaction terms of all variables on the three responses. As in the case verified with MEK, the most important factor is the solvent to oil ratio, while the mixing time does not affect significantly the responses.

Following the same procedure adopted for the extraction with MEK, preliminary tests were performed to assess the effect of the most significant variable (solvent to oil ratio) on the yield, sludge removal and oil loss at different concentration levels of KOH.

Figure 5.9 shows that the general pattern of the three responses when SOR increases is similar to what was obtained with MEK (Figure 5.3). By analyzing

Figure 5.9 (a), it can be noticed that the yield exhibits a behavior more coherent than that presented in Figure 5.3 (a). The reason of this behavior was already explained; basically, the higher is the ratio between solvent and waste oil, higher will be the oil dissolved in 1-butanol, up to a point at which all the base oil is dissolved and thus the yield will stabilize instead of increasing.

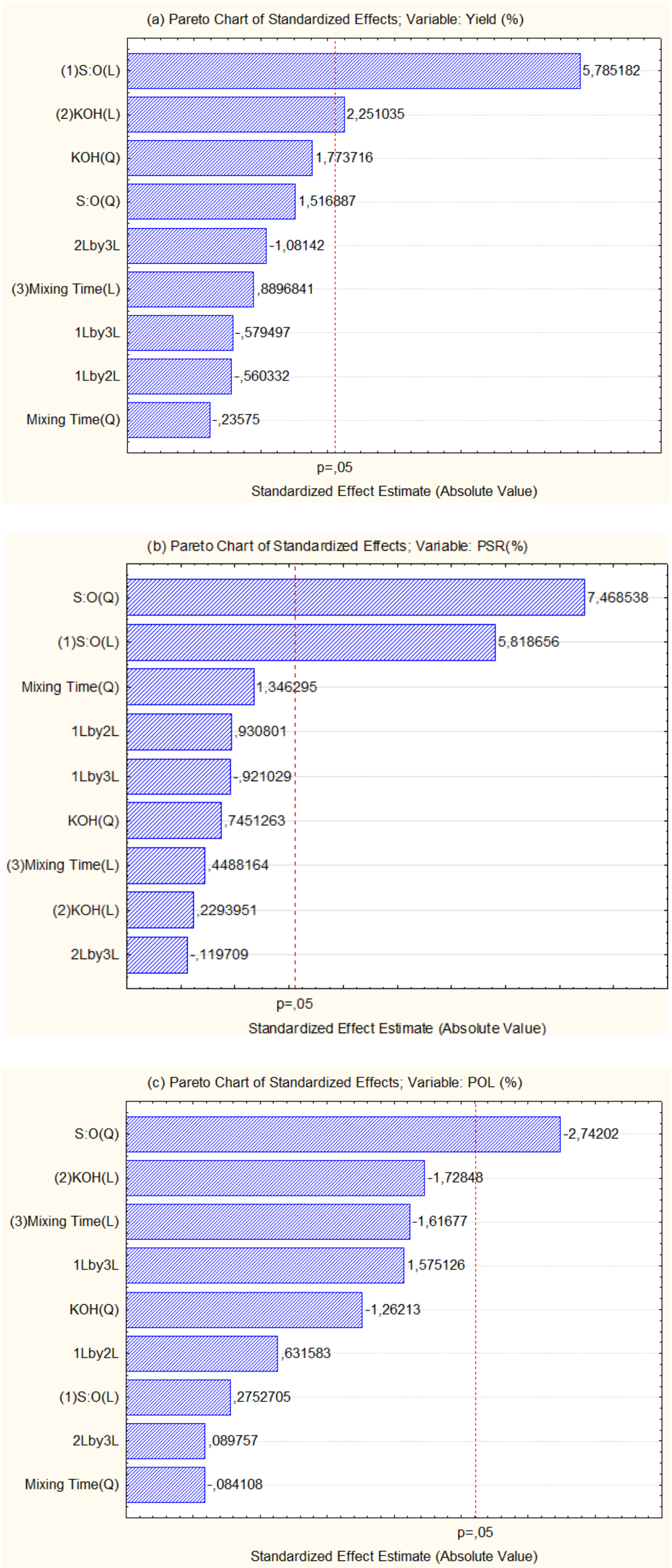


Figure 5.8: Pareto Chart of standardized effects for (a) Yield, (b)PSR and (c) POL.

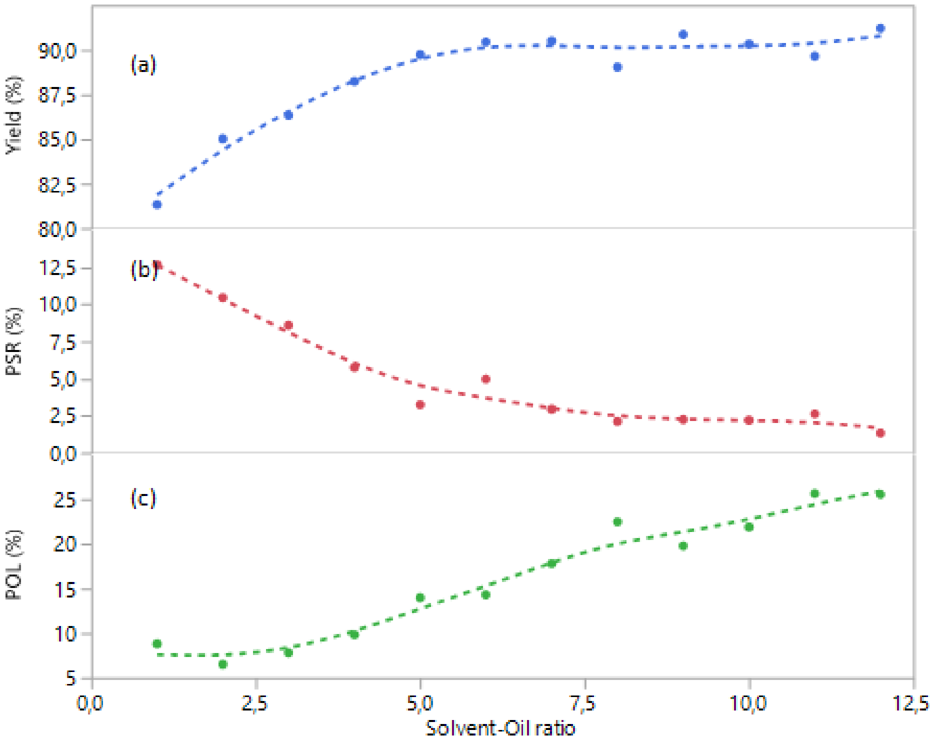


Figure 5.9: General behavior of (a) Yield, (b) sludge removal, (c) oil loss, as a function of SOR

As observed for MEK, the behavior of Yield in

Figure 5.9 is the expected one according to the literature, while PSR and POL is the opposite (Elbashir et al. 2002; Mohammed et al. 2013).

Once again, to overcome these problems different strategies were applied. Some tests were repeated using a Central Composite Design, involving only two process variables (SOR and KOH dosage) and neglecting the mixing time. The temperature of the oil bath was increased to 172°C, and the falcon tubes were dried in the oven at 105°C before the measurements of the wet sludge.

The levels of the variables are the same used for MEK, and are shown in Table 5.3 and the experimental results obtained from the new experimental design are summarized in Table 5.7

Table 5.7: The central composite design applied, showing the operating conditions and the results obtained with 1-butanol.

N° Test	Mass oil (g)	Mass solvent (g)	Regenerated oil (g)	Yield (%)	PSR (%)	POL (%)
1	6.67	13.33	5.85	87.79	8.83	1.90
2	6.66	13.39	5.72	85.90	8.95	1.88
3	6.66	13.33	5.90	88.67	9.27	1.70
4	4.02	16.00	3.55	88.35	7.81	1.05
5	3.99	16.00	3.50	87.56	7.31	2.05
6	4.00	16.01	3.62	90.53	6.87	2.08
7	4.00	16.01	3.66	91.52	7.31	1.90
8	2.87	17.14	2.58	90.13	6.49	1.27
9	2.86	17.14	2.61	91.30	6.78	0.63
10	2.87	17.14	2.69	93.46	6.89	0.63

Figure 5.10 shows the variation of the Yield as function of SOR for three different concentration of flocculant (KOH). In Figure 5.10 (b) and (c) can be observed that the refining Yield increases with increasing SOR up to a point at which it stabilizes. This behavior is not observed in Figure 5.10 (a) where is illustrated the refining yield obtained with pure 1-butanol. The reasons is that the stabilization of the response without the flocculant agent occurs at higher ratios.

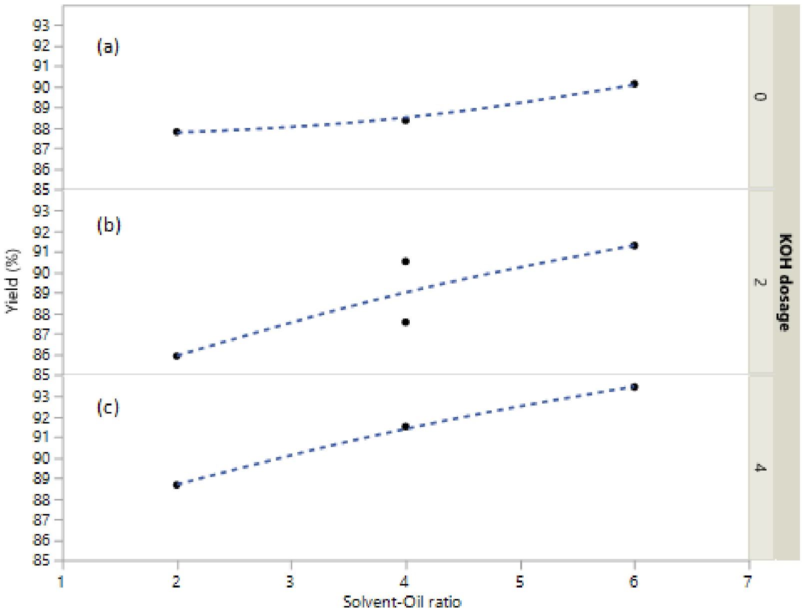


Figure 5.10: Effect of the solvent-oil ratio on Yield with (a) 0 g/L of KOH, (b) 2g/L of KOH (c) 4g/L of KOH

As observed in the tests with MEK, even by changing the experimental design and the levels of the process variables, the behavior of PSR when SOR is changed never assumed the expected trend described by the literature (Omolara et al. 2015; Nimir et al. 1997).

However, the modifications to the experimental design have led to improvements with regard to the results of the POL, as shown in Figure 5.11:

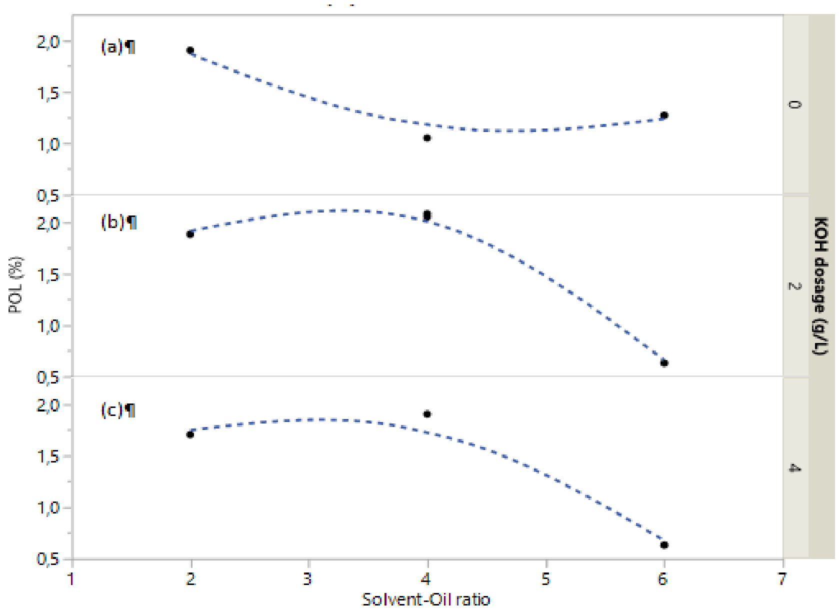


Figure 5.11: Effect of SOR on POL with (a) 0g/L of KOH, (b) 2g/L of KOH and (c) 4g/L of KOH

Figure 5.11 clearly indicates that an increase of SOR led to a decrease of the oil trapped in the sludge. As mentioned above, this can be explained considering that the mutual solubility of the oil in the solvent is enhanced when the SOR increases, and because of that the sludge phase trapped a lower quantity of oil. This trend already observed by Elbashir et al. (2002), is enhanced in Figure 5.11 (b) and (c), where was used the combination of 1-butanol and KOH. The trend observed for POL in Figure 5.11 (a) is a bit dubious. could be due to the fact that without the flocculant agent, impurities are not completely agglomerated and can trap a little quantity of oil in the sludge phase (Yang et al. 2013).

The STATISTICA software was used for regression analysis of the data obtained. The statistical significance of the models was evaluated using the R^2 values, which are reported in Table 5.8, while equations (5.10) and (5.11) report the regression coefficient:

$$Yield(\%) = 85.31690 + 1.03077A - 0.03661A^2 - 1.18607B + 0.29714B^2 + 0.15312AB \tag{5.10}$$

$$POL(\%) = 0.822381 - 0.617738A - 0.101071A^2 + 0.295119B - 0.046071B^2 - 0.027500AB \tag{5.11}$$

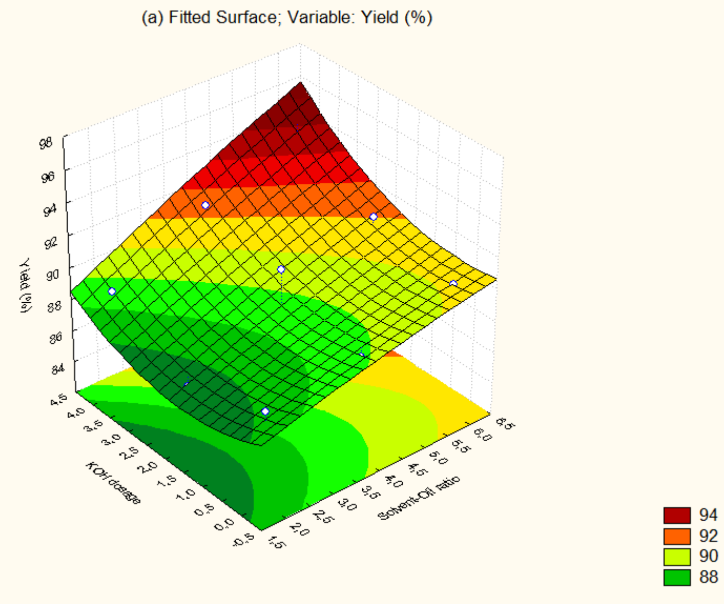
The higher value of R^2observed to Yield suggests a satisfactory reliability of the model by which 87 % of the response variability can be explained by the model.

Table 5.8: Values of R^2 for the responses

Response	R^2
Yield	0.868
POL	0.698

The simultaneous effect of process variables upon Yield and POL during extraction with 1-butanol can be seen in response surface graphs depicted in Figure 5.12.

Figure 5.12 give a good indication of the optimal conditions for the extraction process with 1-butanol. Indeed, to maximize Yield and minimize POL, the best conditions are close to those corresponding to upper levels of the solvent to oil ratio and KOH concentration.



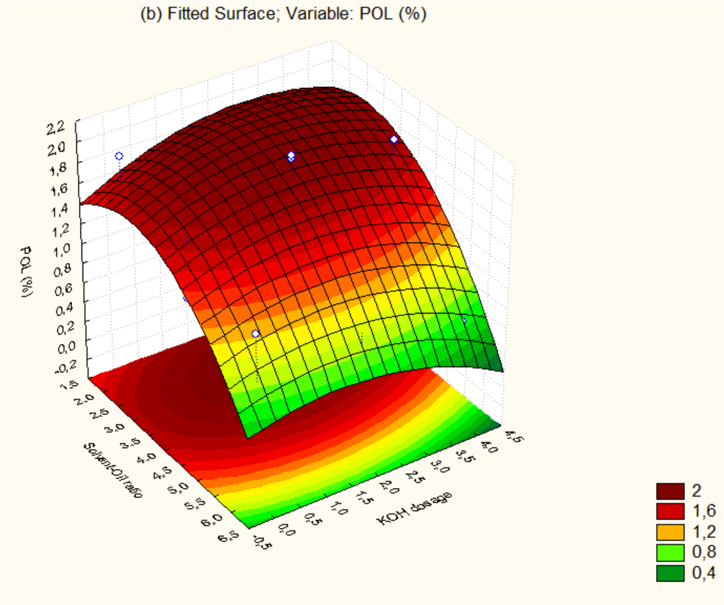


Figure 5.12: Response surface, (a) yield, (b) POL.

5.5. COMPARISON BETWEEN MEK AND 1-BUTANOL

Considering the results obtained for the extraction with MEK and with 1-butanol, it can be stated that in general, the trend of the responses are similar for both solvents.

According to the response surfaces (Figure 5.6 and Figure 5.12), the maximum refining Yield and minimum POL are obtained for the upper values of the SOR and KOH concentration. By observing Figure 5.13 (b) and (c) it can be noticed that the Yield of the base oil obtained with 1-butanol is higher than the one resulting from extraction with MEK when the process is performed combining solvent at SOR of 6 and flocculant agent.

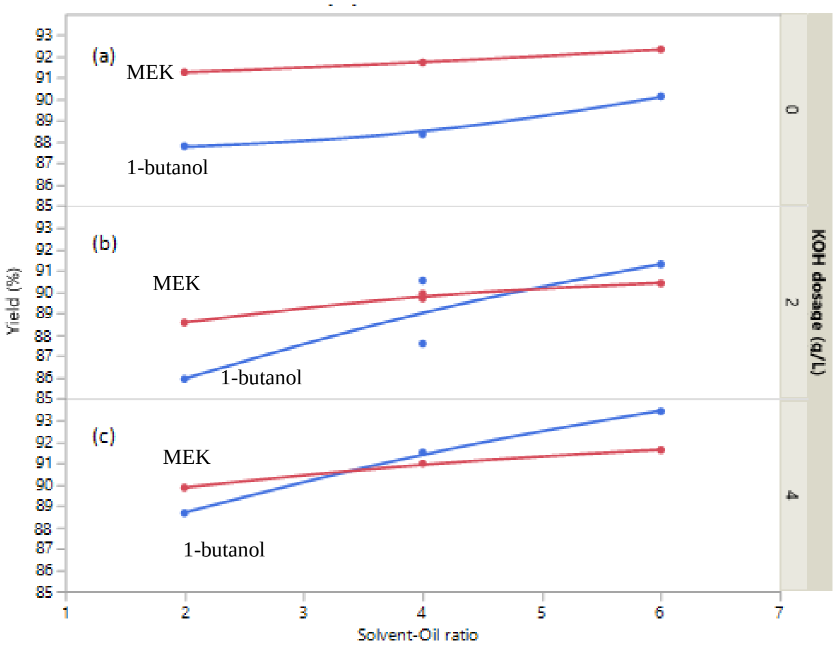


Figure 5.13: Comparison of the refining Yield obtained with (a) 0 g/L of KOH, (b) 2g/L of KOH (c) 4g/L of KOH

In general this trend can be also observed for POL in Figure 5.14.The higher the SOR, lower is the percentage of base oil trapped in the sludge phase. As described for the Yield, KOH enhances the removal of impurities, increasing Yield and decreasing POL. In Figure 5.14 (b) and (c) can be seen that under optimal conditions, the oil loss with 1-butanol is slightly lower than for MEK, proving the best performance obtained by the alcohol.

According to Alves Dos Reis and Jeronimo (1988) and Martins (1997), with 1-butanol it was noticed that the higher KOH concentration in the solvent, led to smaller dimension of the flocculated particles. This behavior was observed only with the alcohols, leading to a better flocculation and removal of contaminants.

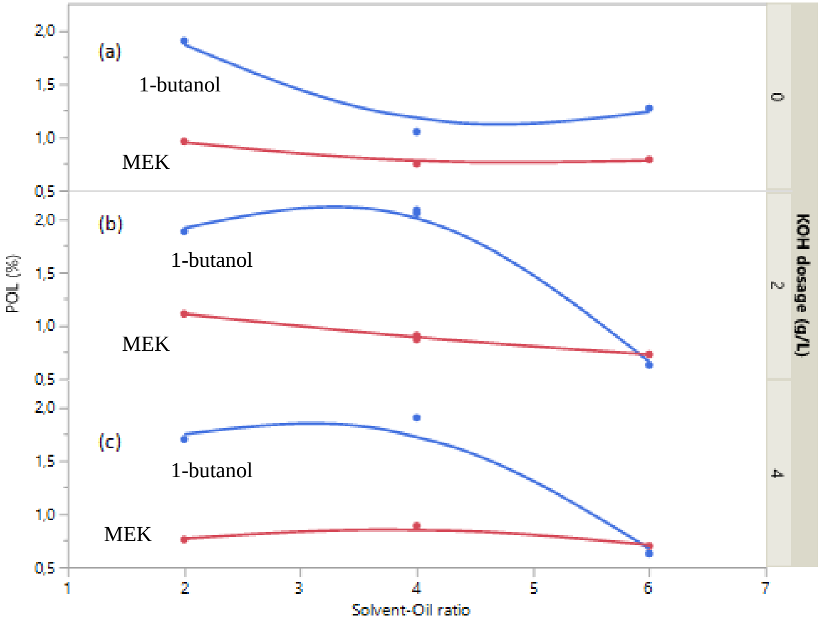


Figure 5.14: Comparison of POL obtained with (a) 0 g/L of KOH, (b) 2g/L of KOH (c) 4g/L of KOH.

5.6. CHARACTERIZATION OF THE EXTRACTED OIL

The characterization of the extracted oil (referred also as base oil) was done through the techniques described in section 4.2. Because of time reasons, it was not possible to perform a complete characterization of the extracted oil using the two solvents. Thus, this characterization was carried out only for 1-butanol which showed the best performance.

The process conditions selected were those able to give the best results in terms of Yield and POL. Therefore, the extraction process to get enough amount of oil for characterization was performed using a concentration of KOH of 4 g/L and mixing time of 15 minutes. To highlighting the importance of the third process variable (SOR), two different ratios were selected: 2:1 and 7:1. In Table 5.9 are shown the viscosity values, viscosity index and TAN measured for the waste oil (OU) and regenerated oil at two different SOR.

Table 5.9: Properties of waste oil and regenerated oil.

Oil	Viscosity at 40°C (cSt)	Viscosity at 100°C (cSt)	Viscosity Index	TAN (mg of KOH/g)
OU	85.04	10.65	109.21	1.87
2:1	36.76	6.50	130.41	0.392
7:1	48.44	8.64	157.60	0.167

The differences are obvious since the samples of regenerated oil exhibit higher values of viscosity and viscosity index (VI), which is a significant advantage in terms of applicability of the oil. It is clear that the oil regenerated using the higher SOR (7:1) has improved characteristics, especially in terms of VI, comparable with base oil.

Regarding the total acid number (TAN), it is noticeable that by increasing SOR, the quality of the regenerated oil is improved, in terms of acid compounds present in the lubricant. In fact, low TAN means that acid contaminants were removed from the waste oil during extraction.

Figure 5.15 show the FTIR spectrum of waste and regenerated oil. The blue curve represents the base oil extracted with a solvent-oil ratio 7:1, the green curve is the base oil extracted with a solvent-oil ratio 2:1 and the brown curve represents the spectrum of the used oil.

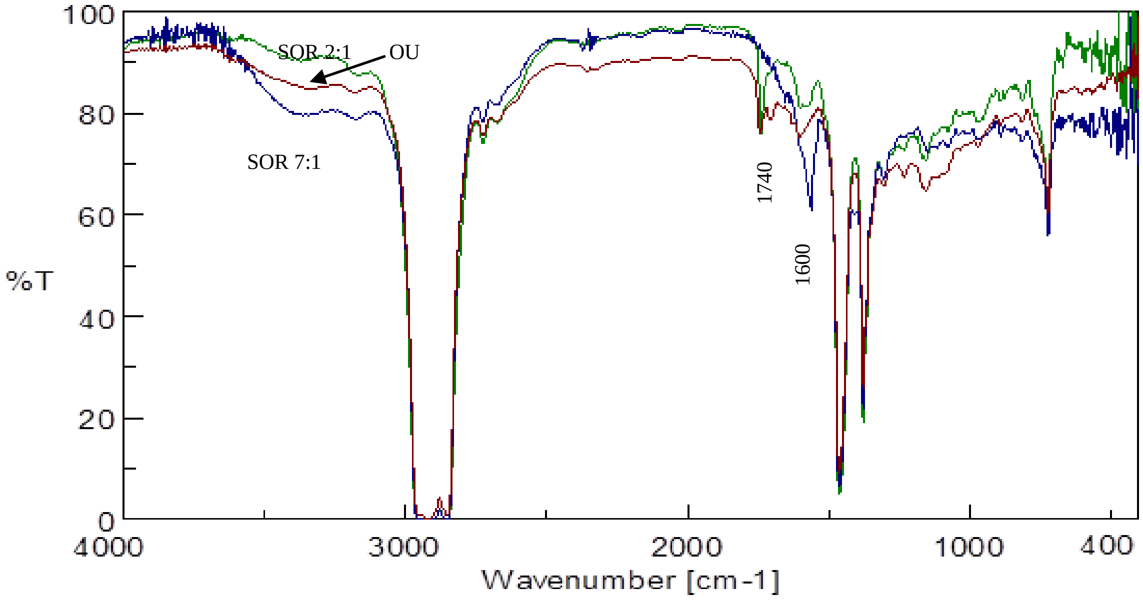


Figure 5.15: Spectra of waste oil (OU) and regenerated oil at SOR 2:1 and SOR 7:1.

In general both used and re-refined oil show peaks in the range 2961-2945 cm^{-1}, that correspond to bonds –CH_2 e –CH_3, and other peaks at 720 cm^{-1}, 1374 cm^{-1} e 1458 cm^{-1} corresponding to vibrations of –CH e =CH. These bonds are characteristic of aliphatic components from the base oil. The spectrum of extracted oil with a SOR 7:1, has a deep peak around 1600 that probably is due to solvent in the oil. In fact, at high ratios the amount of oil is very low with respect to the quantity of solvent, and it is hard to achieve the total evaporation of it. It can be noticed also that at 1740 cm^{-1} and 1710 cm^{-1}, the used oil and the extracted oil with a SOR 2:1 present peaks characteristic of esters and ketones, which are products of oxidations. These peaks are not observed in the case of SOR 7:1, indicating an improved quality of the extracted oil.

A comparison of the metallic content of the extracted oils and of initial used oil can be seen in Figure 5.16. It can be observed that the amount of contaminants decreases with increasing SOR. This is so because increasing SOR increase the amount of impurities that precipitate, and the quality of the extracted oil increases.

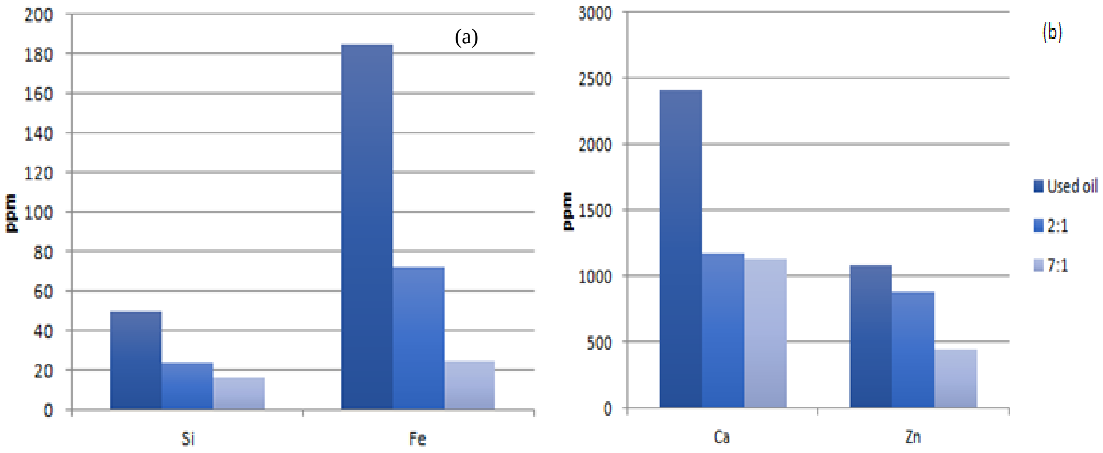


Figure 5.16: (a): Si and Fe and (b): Ca and Zn content of used and regenerated oil at SOR 2:1 and SOR 7:1

6. CONCLUSIONS AND FUTURE WORK

Solvent extraction process has been found to be one of the competitive processes for the regeneration of waste lubricating oil. It allows the separation of reactive components, such as unsaturated hydrocarbons and other contaminants from the waste oil, in order to improve its physicochemical properties and obtain base oil.

In this work the performance of two different solvents, MEK and 1-butanol have been tested, analyzing the response of Yield, PSR and POL, by varying the solvent-oil ratio, KOH dosage and mixing time.

The experimental results showed that SOR is the most important factor, and mixing time has a neglecting effect. Yield revealed the expected behavior, but PSR presented a trend in contrast with other works. Although several attempts were implemented, the study of the sludge removal was put aside, and further investigation will be needed in the future.

Nevertheless, the optimal extraction conditions have been found for the Yield and the POL, by using the response surface methodology (RSM). The results indicated that increasing SOR and KOH the responses increase, up to a point at which both parameters stabilize. Indeed, increasing SOR the amount of base oil that can be dissolved increase, up to a point at which all the base oil is dissolved. At the same time, the flocculation is promoted by KOH, segregating the impurities from the base oil.

The best Yield (93,46%) was obtained with 1-butanol, using 4 g/L of KOH and a solvent-oil ratio of 6:1. In case of MEK tested at the same conditions, the Yield is slightly lower (91,64%). These conditions are responsible also for the best results in terms of POL, 0,63% and 0,70 for 1-butanol and MEK, respectively. The experimental results indicated 1-butanol as the best solvents.

The physicochemical properties of the regenerated oil demonstrated the effectiveness of the extraction process, and confirmed that higher values of SOR improved the quality of the regenerated oil.

It is important to state that the optimal conditions found out in this work should be revised if a different scale is used. In fact, the data obtained are carried out at laboratory scale, disregarding issues related to the costs of solvents and separation operations. At industrial scale should be found a tradeoff between the amount of extracted oil and amount of solvent used in the process, taking into account also of the energy costs related to the evaporation of the solvents.

Thus is possible that the optimal conditions found out in this work could be slightly shifted with a scale up of the process.

The main points to be further explored in future investigations are:

- Explore the possibility of using a combination of both solvents;
- Investigate the behavior of PSR as a function of SOR, to determine the reason why the observed trend is not correct;
- Validate the mathematical models obtained from linear regression analysis;
- Do an economic analysis regarding to obtain a compromise between costs and efficiency of the extraction;
- Fully characterize the regenerated oil, after the extraction process;

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APPENDIX

In appendix are reported the results of the full factorial design with MEK Table A.1 and -butanol Table A.5, and the tables with the regression coefficient of the equations (5.2),(5.3) and (5.4) in Table A.2, Table A.3, Table A.4, respectively. In Table A.6,Table A.7 and Table A.8 are reported the regression coefficient of equations (5.7), (5.8) and (5.9).

Table A.1: Results of the full factorial design (MEK)

SOR	KOH dosage (g/L)	Mixing time (min)	Yield(%)	PSR(%)	POL(%)
1	1	10	95.35	2.98	1.31
1	1	20	91.47	4.91	6.55
1	1	30	93.82	4.55	6.35
1	2	10	94.59	5.03	5.55
1	2	20	94.67	4.99	4.92
1	2	30	91.74	4.87	5.48
1	3	10	93.83	3.06	5.35
1	3	20	94.17	4.45	5.14
1	3	30	91.63	4.08	6.39
3	1	10	90.18	7.05	7.20
3	1	20	89.88	7.04	7.50
3	1	30	90.17	6.51	6.23
3	2	10	92.4	7.39	7.02
3	2	20	94.58	6.79	6.33
3	2	30	93.16	6.67	5.52
3	3	10	91.74	7.49	8.15
3	3	20	91.62	6.58	5.84
3	3	30	93.67	6.91	5.75
5	1	10	93.97	5.58	7.29
5	1	20	91.99	6.59	7.32
5	1	30	94.43	5.58	7.72
5	2	10	93.76	5.52	7.91
5	2	20	94.25	5.72	7.33
5	2	30	92.61	5.72	7.61
5	3	10	93.91	5.98	5.84
5	3	20	94.7	6.50	6.96
5	3	30	96.53	6.32	7.90

Table A.2: Regression coefficient for the yield (MEK)

Yield (%)	Regression Coeff.	Std.Err.	t(17)	p
Mean/Interc.	97.94981	3.91503	25.01892	0.00000
(1)SOR (L)	-3.77194	1.06121	-3.55440	0.00244
SOR (Q)	0.45306	0.14531	3.11782	0.00626
(2)KOH dosage (g/L)(L)	1.61833	2.56397	0.63118	0.53632
KOH dosage (g/L)(Q)	-0.58111	0.58125	-0.99977	0.33144
(3)Mixing time (min)(L)	-0.23737	0.25640	-0.92581	0.36750
Mixing time (min)(Q)	0.00157	0.00581	0.27049	0.79004
1L by 2L	0.24000	0.20550	1.16787	0.25898
1L by 3L	0.03546	0.02055	1.72545	0.10258
2L by 3L	0.02858	0.04110	0.69545	0.49617

Table A.3: Regression coefficient for the PSR (MEK)

PSR (%)	Regression Coeff.	Std.Err.	t(17)	p
Mean/Interc.	-0.27891	1.62460	-0.17168	0.86572
(1)SOR (L)	3.10556	0.44036	7.05226	0.00000
SOR (Q)	-0.45035	0.06030	-7.46854	0.00000
(2)KOH dosage (g/L)(L)	0.55354	1.06396	0.52027	0.60959
KOH dosage (g/L)(Q)	-0.17972	0.24120	-0.74513	0.46637
(3)Mixing time (min)(L)	0.16378	0.10640	1.53939	0.14212
Mixing time (min)(Q)	-0.00325	0.00241	-1.34629	0.19589
1L by 2L	0.07937	0.08528	0.93080	0.36499
1L by 3L	-0.00785	0.00853	-0.92103	0.36992
2L by 3L	-0.00204	0.01706	-0.11971	0.90612

Table A.4: Regression coefficient for the POL (MEK)

POL (%)	Regression Coeff.	Std.Err.	t(17)	p
Mean/Interc.	0.29963	3.33825	0.08976	0.92953
(1)SOR (L)	1.71333	0.90486	1.89347	0.07544
SOR (Q)	-0.08556	0.12390	-0.69050	0.49920
(2)KOH dosage (g/L)(L)	1.28472	2.18623	0.58764	0.56450
KOH dosage (g/L)(Q)	-0.03056	0.49561	-0.06165	0.95156
(3)Mixing time (min)(L)	0.15647	0.21862	0.71572	0.48388
Mixing time (min)(Q)	-0.00067	0.00496	-0.13563	0.89370
1L by 2L	-0.17917	0.17523	-1.02249	0.32088
1L by 3L	-0.01592	0.01752	-0.90835	0.37639
2L by 3L	-0.03167	0.03505	-0.90359	0.37884

Table A.5: Results of the full factorial design (1-butanol)

SOR	KOH dosage (g/L)	Mixing time (min)	Yield(%)	PSR(%)	POL(%)
1	1	10	77.69	11.98	17.49
1	1	20	77.85	7.01	17.14
1	1	30	83.67	12.25	10.30
1	2	10	83.41	13.36	6.81
1	2	20	81.17	15.62	8.24
1	2	30	85.36	11.80	7.23
1	3	10	88.29	3.90	16.21
1	3	20	79.74	15.38	9.15
1	3	30	88.34	5.76	8.42
3	1	10	88.58	8.02	9.63
3	1	20	87.50	8.49	8.89
3	1	30	88.22	9.19	7.01
3	2	10	85.91	9.36	10.91
3	2	20	94.57	10.11	7.32
3	2	30	90.86	8.42	9.48
3	3	10	90.27	9.77	7.33
3	3	20	88.05	9.49	7.37
3	3	30	88.01	9.19	8.02
5	1	10	87.63	7.43	12.51
5	1	20	87.81	7.75	10.36
5	1	30	89.29	7.15	14.09
5	2	10	92.69	6.99	12.07
5	2	20	94.97	8.26	12.83
5	2	30	95.02	7.24	10.63
5	3	10	90.69	8.89	10.03
5	3	20	96.73	7.90	11.83
5	3	30	88.33	7.47	9.72

Table A.6: Regression coefficient for the yield (1-butanol)

Yield (%)	Regression Coeff.	Std.Err.	t(17)	p
Mean/Interc.	59,85407	8,69825	6,88117	0,00000
(1)SOR (L)	6,13583	2,35774	2,60242	0,01859
SOR (Q)	-0,48972	0,32285	-1,51689	0,14767
(2)KOH dosage (g/L)(L)	13,58306	5,69652	2,38445	0,02902
KOH dosage (g/L)(Q)	-2,29056	1,29139	-1,77372	0,09402
(3)Mixing time (min)(L)	0,22143	0,56965	0,38871	0,70231
Mixing time (min)(Q)	0,00304	0,01291	0,23575	0,81644
1L by 2L	-0,25583	0,45657	-0,56033	0,58256
1L by 3L	-0,02646	0,04566	-0,57950	0,56985
2L by 3L	-0,09875	0,09131	-1,08142	0,29461

Table A.7: Regression coefficient for the PSR (1-butanol)

PSR (%)	Regression Coeff.	Std.Err.	t(17)	p
Mean/Interc.	4,37296	7,37693	0,59279	0,56113
(1)SOR (L)	-1,45806	1,99959	-0,72918	0,47582
SOR (Q)	0,02861	0,27380	0,10449	0,91800
(2)KOH dosage (g/L)(L)	4,73819	4,83118	0,98075	0,34047
KOH dosage (g/L)(Q)	-1,40556	1,09522	-1,28336	0,21659
(3)Mixing time (min)(L)	0,52564	0,48312	1,08801	0,29177
Mixing time (min)(Q)	-0,01214	0,01095	-1,10835	0,28314
1L by 2L	0,33875	0,38722	0,87483	0,39386
1L by 3L	-0,00842	0,03872	-0,21736	0,83051
2L by 3L	-0,01083	0,07744	-0,13989	0,89039

Table A.8: Regression coefficient for the POL (1-butanol)

POL (%)	Regression Coeff.	Std.Err.	t(17)	p
Mean/Interc.	29,12954	7,25194	4,01679	0,00089
(1)SOR (L)	-6,02278	1,96571	-3,06393	0,00703
SOR (Q)	0,73806	0,26917	2,74202	0,01390
(2)KOH dosage (g/L)(L)	-7,36792	4,74933	-1,55136	0,13923
KOH dosage (g/L)(Q)	1,35889	1,07666	1,26213	0,22394
(3)Mixing time (min)(L)	-0,33026	0,47493	-0,69539	0,49621
Mixing time (min)(Q)	0,00091	0,01077	0,08411	0,93395
1L by 2L	0,24042	0,38066	0,63158	0,53606
1L by 3L	0,05996	0,03807	1,57513	0,13365
2L by 3L	0,00683	0,07613	0,08976	0,92953