

Investigation of Binary Solvents Performance for Regeneration of Iraqi 15W- 40 Waste Lubricant

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Abstract

The aim of this study was to investigate the effectiveness of binary solvent for regeneration of spent lubricating oil by extraction-flocculation process. The regeneration was investigated by bench scale experiments by using locally provided solvents (Heavy Naphtha, n-Butanol, and iso-Butanol). Solvents to used oil, mixing time, mixing speed and temperatures were studied as operating parameters. The performance on three estimated depended key parameters, namely the percentage of base oil recovered (Yield), percent of oil loss (POL), and the percent of sludge removal (PSR) were used to evaluate the efficiency of the employed binary solvent on extraction process. The best solvent to solvent ratio for binary system were 30:70 for Heavy Naphtha : n-Butanol (N:n-But) and Heavy Naphtha : iso-Butanol (N:iso-But). The optimum solvent to oil ratio or critical clarifying ratio (CCR) were 3.4, and 3.8 for N : n-But, and N : iso-But respectively. The optimized operating mixing time, mixing speed, and temperature which result in, maximum recovered base oil (87.75% and 88.88%), minimum oil losses (8.46% and 3.62%), and maximum sludge removal (5.63% and 6.12%), were (45 min, 700 rpm, 35 °C), and (30 min, 700 rpm, 35 °C) for N:n-But, and N:Iso-But respectively.

Key words: Extraction-Flocculation, Used Oil Regeneration, POL, PSR.

Introduction

Increasing of energy demand associated with increasing the consumption of lubricants, as a result larger amount of used oil produced yearly, and disposal issues raised up [1]. Lubricating oil have to be replaced after served the designated period because chemical turn out along with contaminants accumulation. Lubricating oil considered a highly pollutant agent because it included a percentage of polycyclic aromatic hydrocarbons (PAHs) beside heavy metals (Zn, Pb, Fe), which made it

harmful to environment [2, 3]. After purification, used oil can be used as a fuel, the alternative way of disposal is to recover the base oil from used oil, which seemed more environmental and economic than used the first way, where the amount of used oil required to produce a certain amount of base oil is 9 times less than the that of crude oil required to produce the same amount of base oil [4].

Solvent extraction treatment method of used oil preferred over another treatment methods because it solved, the problem such as acidic

sludge produced which is difficult to disposal, highly metal content of recovered base oil, and high cost due to the required quantity of clay associate with using the eldest treatment acid-clay, which is out of use in developing countries [5]; solved the problems of high cost and loss of oil associated with vacuum distillation-extraction process [6]; also solved the problems associated with using distillation-hydrogenation process such as the difficult hydrogenation step, due to the nature of hertoatoms (H, N, S), possibility of forming potential pollutant dissolved stable beside gaseous compounds, and the cost of catalyst [7, 8].

Solvent extraction process associated with mixing the used oil with suitable solvent at appropriate ratio to recover the base oil and segregate the impurities. The employed solvent is recoverable and usually suitable to be employed in another process [9]. The action of flocculation depends on the characteristics of the particles as well as the fluid-mixing conditions; flocculation of dispersed solid impurities occurring due to destabilization of these impurities. By mixing the destabilized solid contaminants and due to random Brownian motion as well as velocity gradient of these particles flocculation occurred [10, 11].

The chemical composition of used oil is varied and difficult to characterize due to the various service period, and the type and concentration of additives [12]. For this reason using a composite solvent system were applied to eliminate as could as possible of used oil contaminants. Many attempts used a composite solvent in used oil treatment such as, Martins (1997), used a ternary solvent composite of butanol/ isopropanol / n-hexane [13], Durrani et al. (2011), were they used binary system of

solvent composite of two alcohols (isopropanol/butanol) and ketone (MEK) [14], and Mahmood (2015), used a binary system composite of acetone /MEK and acetone/heptane [15].

The main goals of this issue are: suggest an effective binary solvents which result in a good refining of the recovered base oil from Iraqi used lubricant (Al-Duraa 15W-40), determine the critical clarifying ratio (CCR) of solvent to used oil, and investigate the effect of various operating conditions at the CCR on the process key parameters.

Experimental Work

1. Materials

1.1. Used Oils

Al-Duraa (15W-40) used lubricating oil. In order to ensure that the used oil is came from Iraqi crude oil, virgin lubricants were employed in automobile at different operating conditions (1500, 2000, and 2500 Km) and then mixed in a container. This mixture represented the used oil feedstok. The properties of used lubricant oil were measured at the Petroleum Research and Development Center Laboratories /Ministry of Oil/Iraq as shown in Table 1. These measurements were done according to ASTM procedure.

1.2. Solvents

Solvents used in this study were, analytical grade n-Butanol, iso-Butanol (HOPKIN & WILLAMS Ind.), and Heavy Naphtha (produced from Al-Duraa Refinery).

2. Procedure

2.1. Pretreatment

Settling and heating is the pretreatment step have to be made. Used oils were allowed to homogenize and settle in a container so that free

water and any settable suspended solids settled down. After that, the sample was heated to 105 °C to remove any remaining water and light cut contaminants [16].

2.2. Mixing

Used oil and solvent brought in contact together at different ratios (2:1 to 6:1) solvent to oil ratio (SOR), at constant temperature (ambient), mixing time (30 min) and mixing speed (500 rpm) in order to determine the critical clarifying ratio (CCR). At this stage solvent extracted the base oil from used oil, while physical contaminants and chemical contaminants are segregated and settled down. The effect of these solvents were evaluated visually at the end of this stage. If the mixture (solvent and used oil) was separated in two layers (raffinate and extract), then the solvent is efficient, otherwise the solvent inefficient.

2.3. Settling

In order to let the dispersed solid (flocculated) particles to settle down, the well mixed mixture (used oil and solvent), leaved for 24 hours at room temperature. After this period of time two layers would form, the upper one was the extraction solvent and base oil, and the bottom liquid phase was heavier material (contaminants).

2.4. Washing and Drying

After the mixture left to settle for 24 hrs., a sludgy black layer formed at the bottom of the flask. This layer was extracted, weighted, and marked as (W_{wet}). The wetted layer was washed with the same employed solvent to remove any remaining trapped oil with the sludge, then the washed sludge heated to separate the excess solvent, weighted, and marked as (W_{dry}). The percent oil losses (POL) and percentage of sludge removal (PSR)

was calculated according to the following formulas [17]:

$$POL = \frac{W_{wet} - W_{dry}}{W_o} \% \quad \dots(1)$$

$$PSR = \frac{W_{dry}}{W_o} \% \quad \dots(2)$$

Where:

W_o : the initial amount of used oil.

W_{wet} : the wetted sludge.

W_{dry} : the dried sludge.

2.5. Recovery

For recovering the base oil from solvent, the up layer was fed into distillation unit. The recovered solvent can be used directly again. The recovered base oil was marked as (W_{oil}). The recovered base oil will submit to some tests to determine either it can use again or not. In order to calculate the percentage of recovered base oil (Yield), the following formula can be used [9].

$$Yield = \frac{W_{oil}}{W_o} \% \quad \dots(3)$$

Where:

W_{oil} The recovered base oil.

W_o The initial amount of used oil.

Results and Discussions

1. Single Solvents

Figures 1, 2 and 3 shown the effect of solvent extraction process on, POL, PSR, and the percentage of base oil yield as a function of the solvent: used oil ratio (SOR), were calculated by using Equation 1, 2 and 3 respectively; at ambient temperature (25 ± 2 °C), 500 rpm, mixing speed, and 30 min, mixing time. The base oil yield was increased, while the POL and PSR were decreased with increasing SOR, for all systems containing used oil and heavy naphtha, n- butanol, or iso-butanol solvent, with different magnitude.

Figure 1, shown that heavy naphtha solvent had the highest recovered base oil practically (91%), followed by n-butanol (90%), and iso-butanol (86%). Figure 2 verified that the solvent heavy naphtha had the lowest percentage of oil loss practically (1.38%), followed by n-butanol (6.52%), and iso-butanol (6.49%). Figure 3 verified that the solvent iso-butanol had the highest percentage of sludge removal practically (10.61), followed by n-butanol (2.66%), and heavy naphtha (0.44%). The various in the key parameters percentage (Yield, POL, PSR) is caused by the difference of solubility of the base oil in these solvents. Heavy naphtha yield percentage was the highest because of the low difference in solubility parameters between the used oil and heavy naphtha. As described by Hildebrand [17], the smaller difference in solubility parameters of two compounds, the higher miscibility between them. With respect to n-butanol and isobutanol, n-butanol resulted in an efficient extraction performance rather than isobutanol. This behavior could be related to the carbon main chain magnitude which caused difference in molecular interaction of the solvent and the used oil and the solvent molecules configuration.

These results in respect of the base oil yield and POL in agreement with the findings of Elbashir et al., Hamed et al., and Hussein et al. [5, 9, 18], but the PSR results disagree with the findings of DURRANI et al. 2012 and Aremu et al. 2015 [12, 1], because it indicated by the experiment for any solvent whether it was polar, or hydrocarbon with increasing SOR more of sludge would dissolve correspondingly. This behavior can be attributed to increase the solvent

amount would increase the affinity, as a result.

2. Binary Solvents

The investigated binary solvents were heavy naphtha : n-butanol and heavy naphtha : iso-butanol. Three different ratios, (40:60), (30:70), and (20:80) of solvent to solvent were studied.

The behavior of binary solvents were same as for the single solvents i.e. the base oil yield was progressively increased with increasing SOR, while the POL and PSR were decreased with increasing SOR due to more of sludge would dissolve and/or disperse in the mixture with increasing SOR as indicated in Figure 4, 5 and 6, for the yield, POL, and PSR respectively. A high yield was obtained with low POL and good PSR, at low SOR which would minimize the solvent used in the process and decrease the operation cost; this consider as a valuable advantage of binary solvent to be used.

By examining the results shown in Figure 4, it is verified that the highest base oil can be recovered at 30:70 solvent to solvent ratio for both of the binary solvents practically (95.5%), and (99.8) for heavy naphtha : n-butanol., and heavy naphtha : iso-butanol respectively; the result shown in Figure 5 verified that the lowest POL, could be achieved by 20:80 solvent to solvent ratio for heavy naphtha : n-butanol solvents practically (3.33%), and (30:70) for heavy naphtha : n-butanol solvents practically (5.9%); while Figure 6 verified that the highest PSR can be achieved at 20:80 for heavy naphtha : iso-butanol (6.7%), and 30:70 for heavy naphtha : n-butanol (7.11%).

The optimum solvent to used oil ratio which called the critical clarifying ratio (CCR), were calculated graphically as described by Elbashir [9]. Figure 7 shown that the CCR value

for N:nBut is 3.8 and for N:iso-But is 3.6, at 30:70 solvent to solvent ratio, which were the best binary solvent

composition gave the best possible results (higher base oil yield, lower POL, and higher PSR).

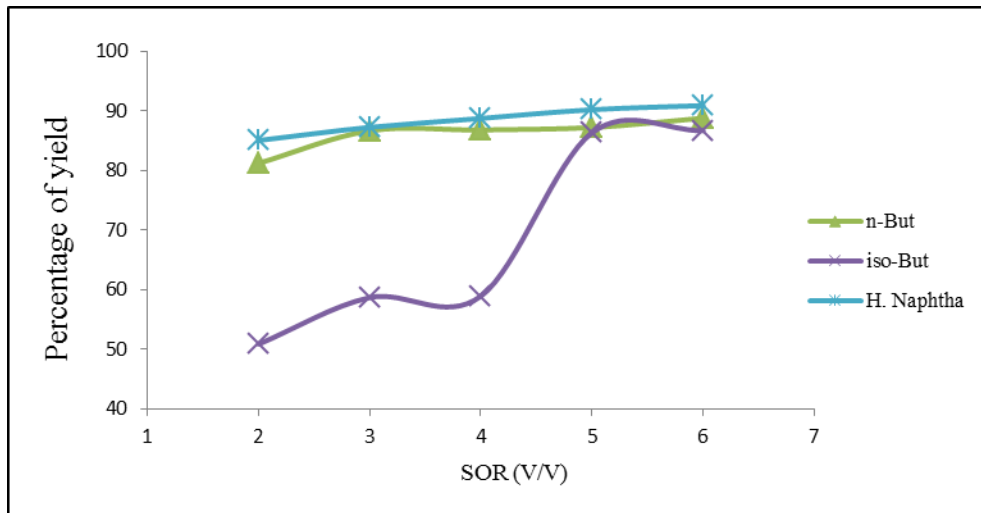


Fig. 1: The effect of single solvent:oil ratio on the percentage of base oil yield

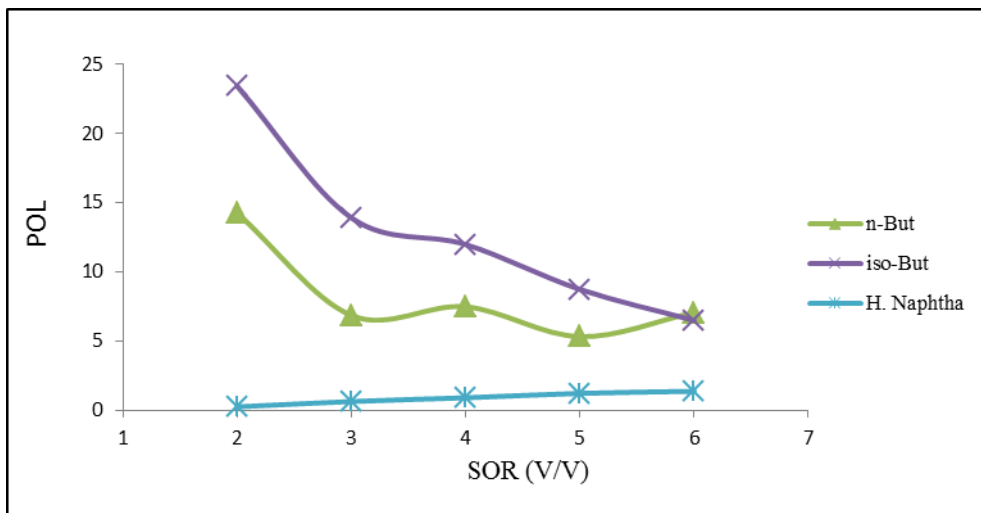


Fig. 2: The effect of single solvent:oil ratio on the POL

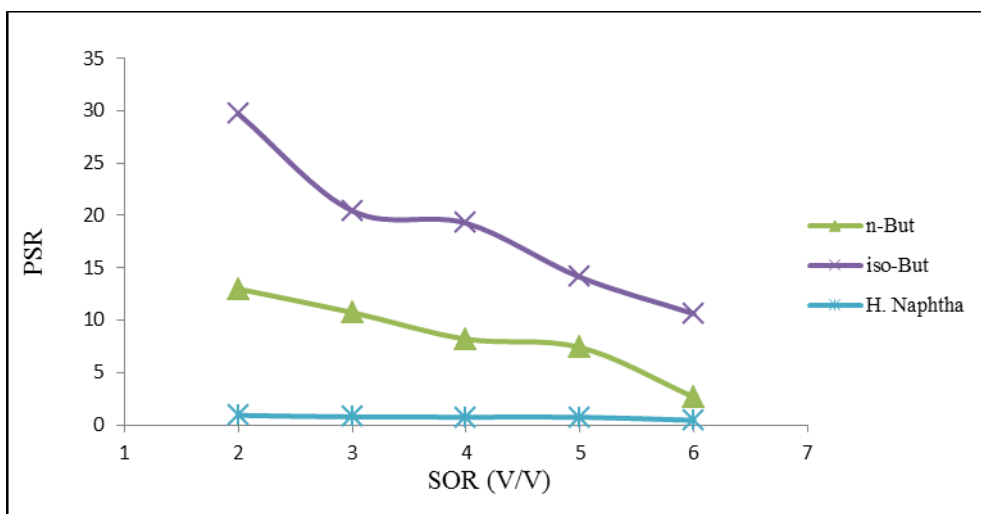


Fig. 3: The effect of single solvent:oil ratio on the PSR

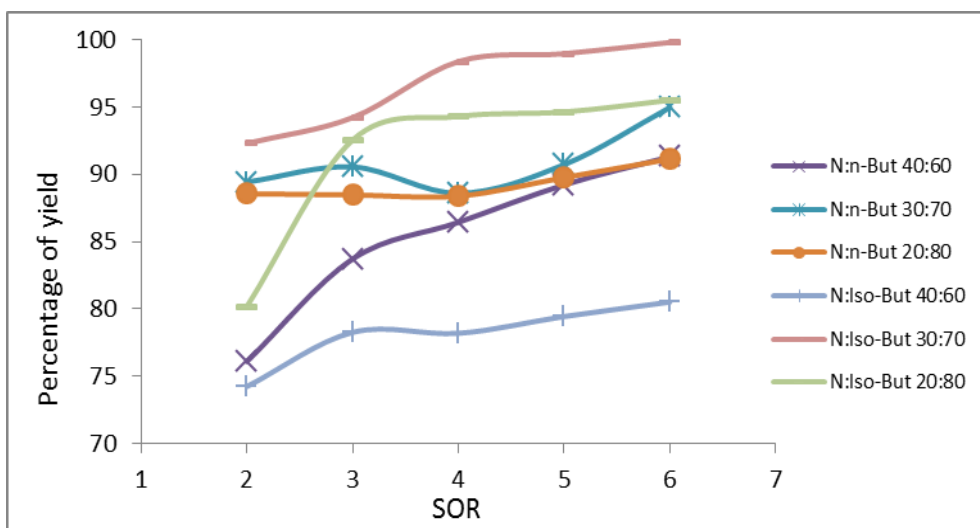


Fig. 4: The effect of binary solvent:oil ratio on the percentage of base oil yield

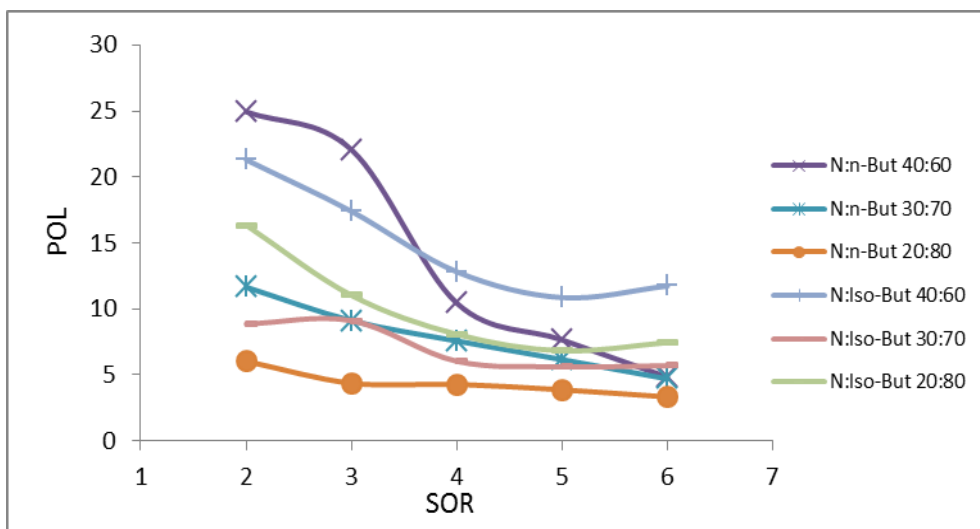


Fig. 5: The effect of binary solvent:oil ratio on the POL

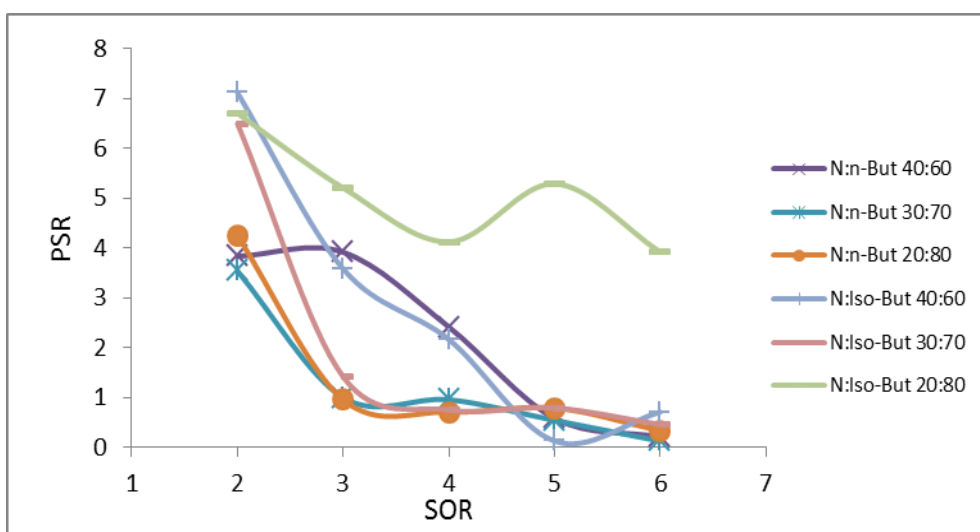


Fig. 6: The effect of binary solvent:oil ratio on the PSR

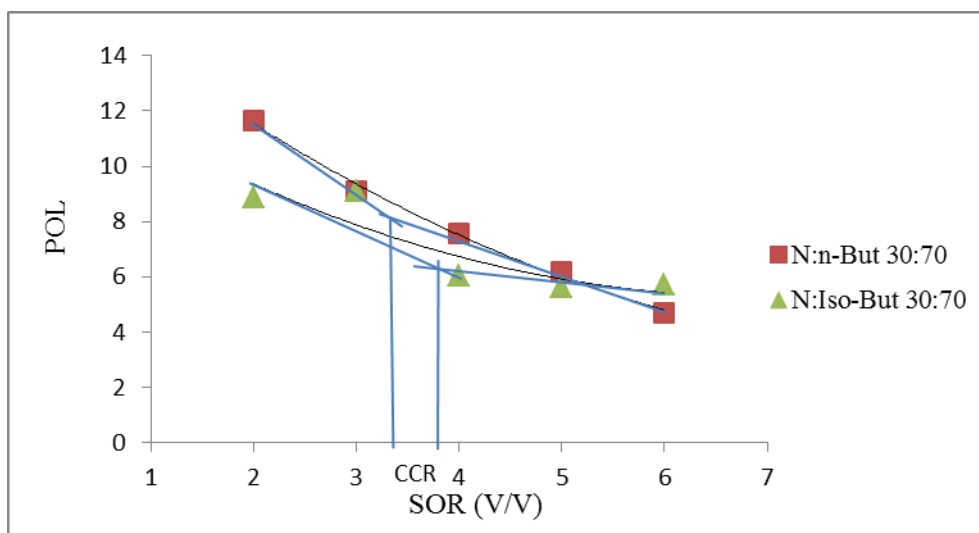


Fig. 7: Graphical determination of critical clarifying ratio (CCR) based on percentage of oil loss POL

2.1. Effect of Mixing Time

At optimum solvent : oil ratio (CCR), the mixtures were mixed by a magnetic stirrer for 15, 30, 45, and 60 minutes at ambient temperature and constant mixing speed 500 rpm. The effect of mixing time for the two binary solvents on POL and PSR indicated in Figures 8 and 9 respectively.

With increasing mixing time, the POL were correspondingly increased clearly recognized, as a result large portion of base oil cannot be separated. These results are in agreement with Hussein et al. [19]. The best mixing time which given, in simultaneously, maximum sludge removal and minimum oil losses is (45 min) for N:n-But, and (30 min) for N:Iso-But.

2.2. Effect of Mixing Speed

At optimum solvent : oil ratio (CCR), the mixtures were mixed by a beyond (30 min) for N:n-but and N:iso-but.

This behavior can be attributed to that the more mixing time, the more of recoverable base oil trapped with sludge formed during mixing period, for this reason the PSR was increased because the same solvent was used, and other parameters were constant. The inflection in the curves in Figure

8, were due to at low mixing time the two layers were not magnetic stirrer at 300, 500, 700 and 900 rpm mixing speed at ambient temperature and at best mixing time experimentally obtained.

The effect of mixing speed for the studied binary solvents on POL and PSR indicated in Figures 10 and 11 respectively. show that with increasing mixing speed, POL and PSR correspondingly increased until 700 rpm. Further increasing led to decrease POL and PSR. This behavior could be explained as, with increasing mixing speed the frequency of collision of impurities increased correspondingly; this would lead to raise POL and PSR. Rising of mixing time more than 700 rpm would act in opposite way i.e. this increment lead to dissociation of flocculated impurities during mixing period, that way the curvature appeared.

The inflection in heavy naphtha: iso-butanol curve in Figure 10 can be attributed to the presence of iso-butanol. Where at low mixing speed the two layers were not completely separated, and more of base oil trapped with inefficiently flocculated particles. The best mixing time which given, in simultaneously, maximum sludge

removal and minimum oil (700 rpm) for both of studied binary solvents.

2.3. Effect of Temperature

At optimum solvent : oil ratio (CCR), the mixtures were mixed by a magnetic stirrer, with best mixing speed and mixing time experimentally obtained; at various temperatures 25, 30, 35, and 40 °C. The effect of temperature for different binary solvents type on POL and PSR indicated in Figures 12 and 13 respectively. The solubility and affinity increase with increasing of temperature, for this reason POL and PSR decreased with increasing temperature due to more of impurities dissolved and/or dissociated with recovered base oil. The best mixing time which given, in simultaneously, maximum sludge removal and minimum oil losses was (35 °C) for both of studied binary solvents. These results are in agreement with the

finding of Hussein et al. and Durrani et al. [19, 12].

The results indicated in Table 1 have been obtained at the best operating values of mixing time, mixing speed, and temperature, for each optimum solvent : oil ratio (CCR) of the binary solvents which were experimentally found as previously expressed. Decreasing of specific gravity value indicates that aromatic compounds and solids have been removed [12]. Reducing the viscosity index (VI) value means that the nonmetallic polymeric viscosity index improvers separated out [20]. Reduction of Ash content value shows the presence of metallic impurities which is reduced by 45-55% in extracted oil. Lowering ash content value indicates that dust, metals products, or products raised from the additives that contain metals have been removed.

Table 1: Properties of used oil and recovered base oil at the best conditions

Properties	Used oil	Recovered base oil	
		N:n-But	N:iso-But
Specific gravity at 15°C g/cm ³	0.8934	0.8802	0.8803
Viscosity at 40 °C ,cSt	117.02	44.893	26.982
Viscosity at 100 °C, cSt	15.134	7.197	5.096
Viscosity index (VI)	134.4	121.2	118.2
Ash content (wt%)	1.0511	0.6070	0.5767
Total base number (mg HCl/g oil)	0	0	0
Total acid number (mg KOH/g oil)	3.5839	2.8542	2.1786
Yield (%)	-	87.75	88.88

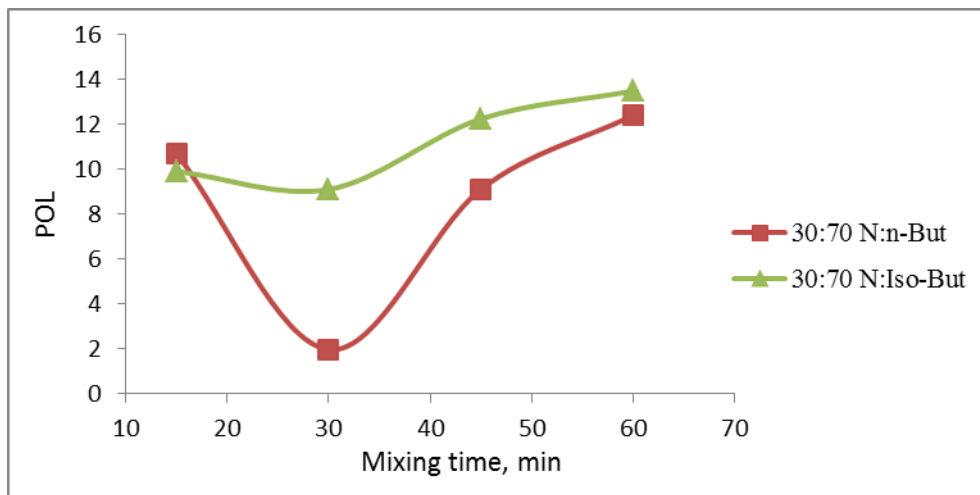


Fig. 8: The effect of mixing time on percentage of oil loss POL for binary solvents

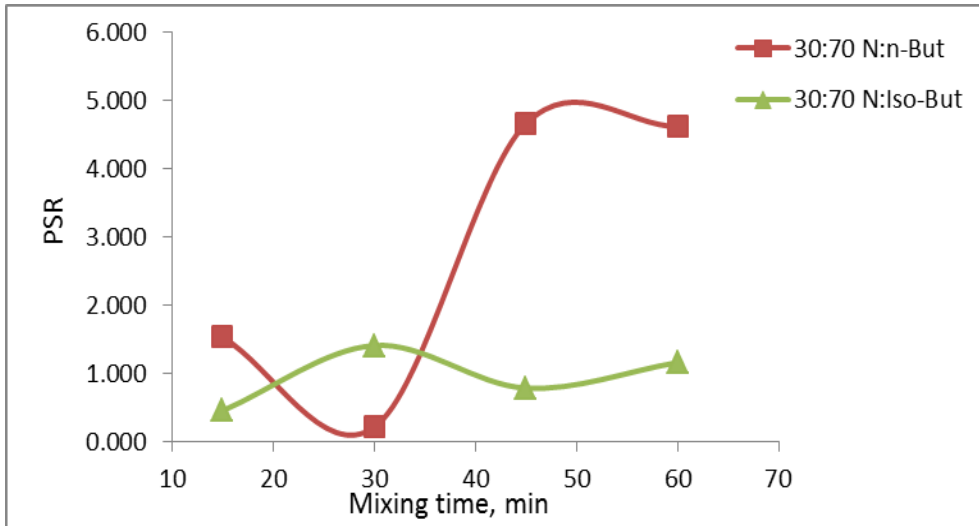


Fig. 9: The effect of mixing time on the PSR for binary solvents

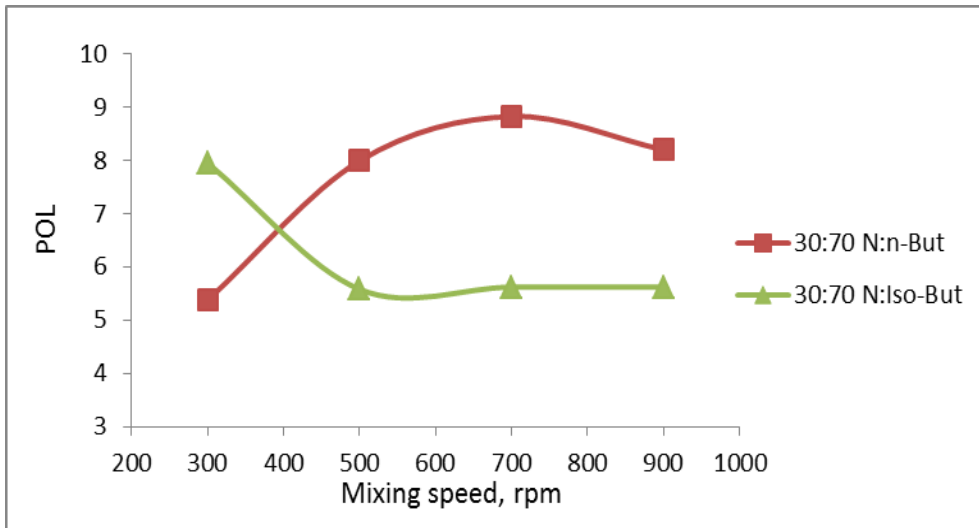


Fig. 10: The effect of mixing speed on the POL for different binary solvents

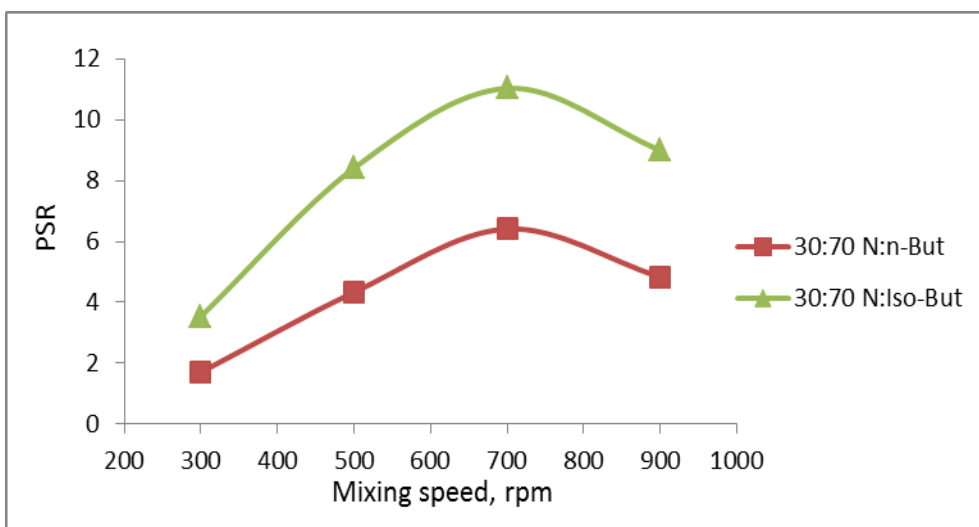


Fig. 11: The effect of mixing speed on the PSR for different binary solvents

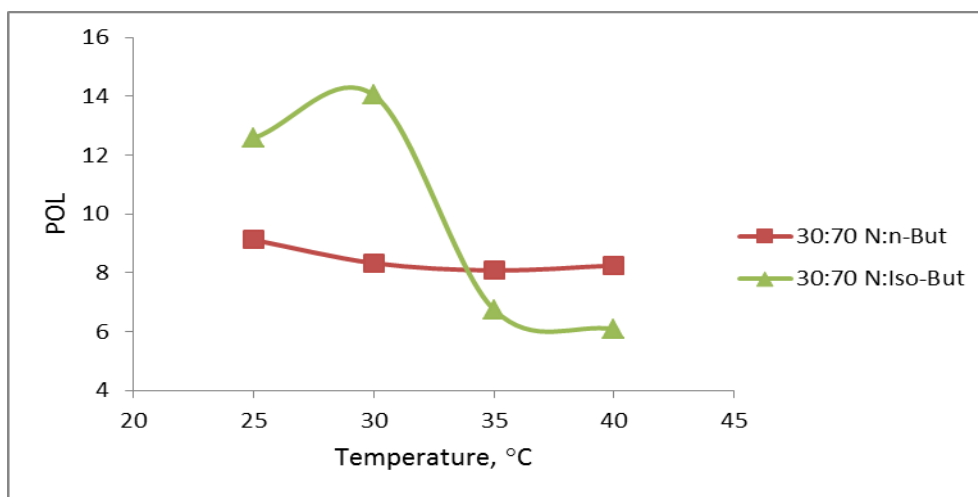


Fig. 12: The effect of temperature on percentage of oil loss POL for binary solvents

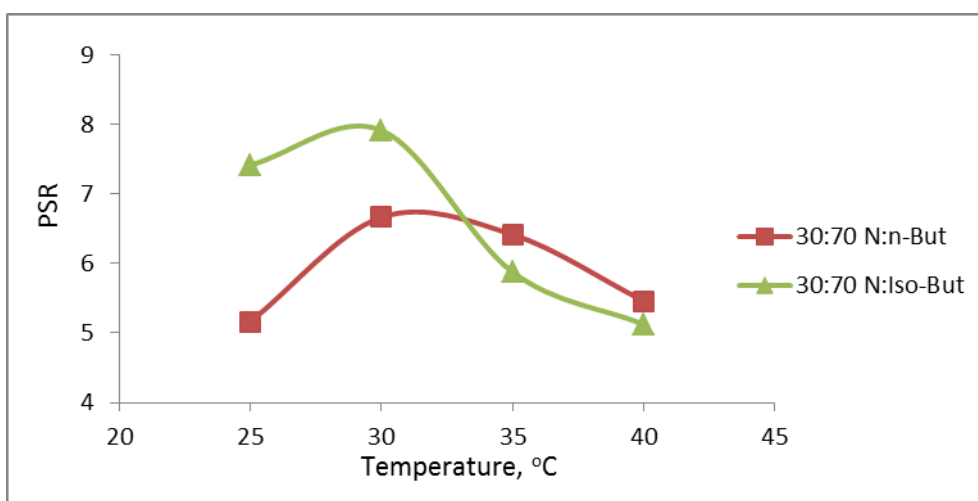


Fig. 13: The effect of temperature on percentage of sludge removal PSR for binary solvents

These results are better in performance and cheaper in composition than those obtained by Durrani et al. [12], where they recovered 80% of the base oil from Iraqi spent oil by using 0.25 isopropanol/0.35 nbutanol/0.40 MEK composite solvent.

Conclusion

The studied binary solvents were good in the process of regeneration of waste oil and cheap as heavy naphtha available locally. N:iso-But showed a better performance than N:n-But where, N:iso-But gave a lower value of viscosity index (VI), ash content, and TAN; in addition the yield percentage were higher than N:n-But.

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