Regeneration of Used Oils by Red Mud and DESs (Reline)

W M Saleh1, R Z Al-Khayat2, Sh M Saied3, A M SYassin4 and F Fadil5

1, 2, 4, 5 Dept. of Chemical Industries, Institute of Technical, Mosul, 3Dept. of Medical Laboratories Technique/ Al-Noor University College, Mosul

Email: 1 wijdan.m.salih@ntu.edu.iq

Abstract To regeneration of oils which are used in cars engines to lubricate its moving parts, and to get rid of highly contaminants which must be separated to reuse the engine oils. In the column chromatography, the waste oil was treated as mobile phase (eluent) with petroleum ether (40-60°C), while the red mud (alhuor) is a stationary phase for adsorbed the impurities. The effect of the new method using deep eutectic solvent (DESs Reline) as a kind of ionic liquids to help extract impurities by adsorption (choline chloride and urea). Moreover, some thermal and physicochemical properties like density, thermal and electrical conductivity, ash percentages, viscosity, specific gravity and pH values were determined. Values were determ. using TGA for blank oil for comparison and differential scanning calorimetric analyses (DSC).

Keywords: Reline, oils, choline chloride, physicochemical properties, waste oils

1.Introduction

Enormous amount of cars oils is considered as destructive waste into the environment in Mosul (the main city in Ninavah/ Iraq), and discarding of used oil in Tigris river, which produces complications not only the water contamination (the only source of people drinking in the area) but also destructive to river life. One gallon of engine oil approximately pollute a million gallon of water including plants [1]. Waste oil used in cars engines to lubricate the moving parts of engine, but it picks up highly contaminants compounds which must be separated in order to reuse the engine oil [2]. So to prevent undesirable properties in engine oil, many additives are used. The laboratory recycling of waste oils depends on the procedures of the refining and chemicals used in these procedures and depend on the type of used oil also, in this paper we will use deep fusion solvent which is a new method (DESs) as a kind of ionic liquid is used to help extract impurities by adsorption. Deep eutectic solvents (DESs) are extensively recognized as a novel type of ionic liquids (ILs) since they share many features and properties with ILs. Deep eutectic solvents (DESs) and ILs have been used mutually in the literature though it is essential to indicate that these are really two different types of solvent [3]. DESs are formed from a eutectic mixture of Lewis or Brønsted acids and bases which can include anionic and/or cationic species; in disparity, ILs are formed from systems composed primarily of one type of discrete anion and cation. It is explain here that the chemical properties of DESs and ILS suggest
application areas which are significantly different although the physical properties of DESs are similar to other ILS [4]. The investigation into DESs has intensified in this decade, ever since the possible for new chemical knowledges was grasped, they have recommended that choline chloride based DESs and Bronsted-Loury acid (hydrogen donor) were effective to remove free glycerol from palm-oil [5]. This waste oil can be distilled into diesel fuel or marine fuel in a process similar to oil re-refining, but without the final hydrotreating process [6]. Paul [7] define the used oil re-refining as the process of restoring used oil to new oil by removing chemical impurities and heavy metals using reclaimed waste lubricating by hydro treating after washing with a polyglycol ether [8]. In 1998, Al-Khazraji used different thermally activated clays which gave best results of reclaiming of used lubricating oils when they were treated with diluted hydrochloric acid [9]. In current work it is the first time to use ionic liquid type of DESs (Reline) in recycle process of oil re-refining, which was only used by modelling and simulation of CO\textsubscript{2} removal from model shale gas along with the physicochemical properties of DESs, which were employed for the modelling and simulation of CO\textsubscript{2} removal studies [10].

2. Materials and Methods

Iraqi Red mud (alhuor), Petroleum ether 40-60 °C, Urea, Choline chloride and Engine oil (new) and used.

2.1 Instruments

The instruments used are electrical conductivity, Weiss – Techn. Werk Statlen, WTW). LBR and pH meter, Philips. TGA and DSC analysis were done by scanning TGA using Horizontal balance and carried out using Mettler-Toledo TGA/ DSC star system in pottery (silica) crucibles at temperatures ranging from (25 to 600°C) with heating rate of (20°C/min) under air atmosphere.

2.2 Preparation of choline chloride – urea DESs (Reline)

A mixture of choline chloride (1 mole) and urea (2 mole) is heated and stirred at 80-100 °C until a clear solution is beginning to form[11]. The product was cooled and used without any purification. The freezing point of the product is 12°C [12].

2.3 Activation of red mud (Al-Khazraji,1998)

The red mud is grinding very well, then it is washed in a sink with water for many times. The resulting mud is draying in microwave oven, then grinding again and is saved in 80 mesh size save. The resulting particles are washed with water, heated in oven at (100 – 120 °C) and then heated in another oven at (600- 800°C).

2.4 Setting the column chromatography

A column was packed with the red mud (absorbent)(about 30 gm) into a cylindrical glass with size (2*30 cm) [13]. The base of the tube contains a glass wool pad to grip the solid phase in place. A solution of oil (20ml.) and DESs (Reline) in petroleum ether (50ml.) ‘Table 1’ was added. Then, the used oil was eluted from the top of the column and 90% of the mixture solvent (64ml. was received from the tap control. This is a simple laboratory column which runs by gravity flow which can be increased by extending the solvent (petroleum ether) filled column above the top of the stationary phase or decreased by the stopcock controls’ Figure 1’.
Table 1. The amounts of DESs (Reline) used.

| Sample No. | Type of oil | Weight of DESs (Reline) (gm) |
|------------|-------------|-------------------------------|
| 1          | fresh       | 1.5                           |
| 2          | fresh       | 2.5                           |
| 3          | fresh       | 3.5                           |
| 4          | fresh       |                               |
| 5          | regenerated |                               |
| 6          | Regenerated | 1.5                           |
| 7          | Regenerated | 2.5                           |
| 8          | Regenerated | 3.5                           |

Table 2. DSC results for analyzed with (without) DESs (Reline) oil samples (which isolated from oxygen).

| Sample No. | DSC Results (°C) | Exothermic peaks | Endothermic peaks |
|------------|------------------|------------------|------------------|
| 5          | 275              |                  | 313              |
| 6          | 282              |                  | 328              |
| 7          | 290              |                  | 328              |
| 8          | 294              |                  | 340              |

3. Results and Discussion
The reaction of quaternary ammonium salt choline chloride and urea is atom efficient since all the atoms present in the starting materials are incorporated in the products DESs (Reline), as in equation 1, the preparation of DES in ethanol [14].

While red mud is a stationary phase for adsorbed the impurities, mobile phase (eluent) is petroleum ether (40-60°C) because it is a solvent used to move the recycle oil through the column. It is selected for two reasons. First, it's retention factor value of approximately 0.2 - 0.3 for diminish the time and the amount of eluent to run the chromatography, and the latter is the different impurities in the used oil can be separated effectively. Chromatography is an important characteristic that affects the oil’s ability to transfer heat from the engine is its thermal properties, the increasing of the values of thermal conductivity (k) of recycle oil samples (5-8) (which is the measure of their abilities to conduct heat) to 35.83211267x10^5 cal.cm^-2.sec^-1 for sample No (8) of the highest amount of Reline (3.5 gm) than that of standard (new) oil 33.73493976 *10^5 cal.cm^-2.sec^-1. Also, specific heats of recycle oil samples (5-8) were only less than the unused samples 1-4 by only less than 0.03°C cm^-3(25°C) (Table 3)the oil transfers heat more efficiently, the higher the thermal conductivity and specific heat[15]
Table 3. The Physical properties of the new and used oil:

| Sample No. | Density (gm .cm\(^{-2}\)) | Thermal conductivity (cal.cm\(^{-2}\).sec\(^{-1}\).°C *10\(^5\)) | Electrical Conductivity (Ohm.cm\(^{-1}\) *10\(^8\)) | Ash content % | Viscosity (25°C) Poise | Specific heat (25°C) c. cm\(^{-3}\) | pH |
|------------|-----------------------------|-------------------------------------------------|---------------------------------|---------------|------------------------|---------------------------------|-----|
| 1          | 0.830                       | 33.73493976                                     | 0.65                            | 0.18          | 3.1428                 | 0.50049                         | 6.51 |
| 2          | 0.826                       | 33.88000                                       | 0.66                            | 0.0           | 3.233                  | 0.498078                        | 6.89 |
| 3          | 0.86                        | 34.72069479                                    | 0.85                            | 0.0           | 3.210                  | 0.486018                        | 6.59 |
| 4          | 0.81                        | 34.45923457                                    | 0.75                            | 0.0           | 2.998                  | 0.48843                         | 6.98 |
| 5          | 0.85                        | 34.763822609                                   | 1.08                            | 1.23          | 2.778                  | 0.485415                        | 8.14 |
| 6          | 0.784                       | 35.69500000                                   | 0.93                            | 1.03          | 2.861                  | 0.472752                        | 8.10 |
| 7          | 0.798                       | 35.06877193                                   | 0.92                            | 0.39          | 2.911                  | 0.481194                        | 6.91 |
| 8          | 0.781                       | 35.83211267                                   | 0.82                            | 0.54          | 2.678                  | 0.470943                        | 6.70 |

Heat transfer happens at a lesser degree in sample (5) of low thermal conductivity than in other samples (6-8) of high thermal conductivity. For instance, samples typically have high thermal conductivity and are very efficient at conducting heat. Sample No. 7 had the best neutralizing value of pH = 6.91 of all other regenerated samples. The acidity of engine oils favors the neutral pH. The polar nature of DESs (Reline) has therefore shown to decrease the electrical conductivity of waste oil \(0.26-0.15\text{ohm cm}^{-1}\). Also, as amount of DESs (Reline), the polar nature increases from 1.5-2.5 gm as viscosity increase from 2.861 to 2.911 Poise, more viscosity means thicker the oil (at higher temperatures, thick oils have more renitence to shearing and losing film strength and these best values indicate that the regenerated oils show minimum contamination). These results come with agreement of ash content percentage which is also 0.39% for sample (7) which is the best oil purity (ash content is very important factors). Specific gravity in cal. / gm °C. Thermal gravimetric analysis (TGA) is measure the change in weight during heating or cooling, it studies of recycle samples show that sample No (5) without DESs (Reline) and sample No. (6) with 1.5 gm verifies less stability at 279°C and 281°C, respectively, with only 10% of weight loss at these temperatures as shown in ‘Figure 2’ and ‘Figure 3’. The same study indicates that samples (7 and 8) of only (1.5 and 2.5 gm) DESs respectively, ‘Figure 4’ and ‘Figure 5’ verified more stability at 300°C with only 10% of weight loss at this temperature.
Similar to TGA, differential scanning calorimetric analyses (DSC) are valid tools in the study of the thermal and oxidative stability of drying oils [16]. DSC analysis can be fit for the estimate the sample stability and the calculation of the film formation (the very first stages) since oil layers have been painted out. The differential scanning calorimetry (DSC) is measuring the absorbed or released heat during heating or cooling. The DSC data shows Table 2, ‘Figure5-8’ an exothermic and endothermic peaks and the decreases in the heat generation is due to decreasing of unburned impurities (such as aromatic hydrocarbons) in the recycle oil. The maximum amount of DESs with sample No (8) gives larger peak of endothermic heat 340°C[17]. The results of these regenerated samples, Sample No (7) of (2.5gm) of DESs (Reline) gives the best result.
4. Conclusion
The methodology presented in this work was succeeded in the removal of waste materials and thus regenerate most properties of the engine lubricating synthetic oil for its reuse. This was achieved by using column chromatography, the waste oil was treated as mobile phase (eluent) with petroleum ether (40-60°C), while the red mud is a stationary phase for adsorbed the impurities. The effect of this new method of using deep-eutectic solvent (DESs Reline) as a kind of ionic liquids to help extract impurities by adsorption (choline chloride and urea). Moreover, sample No (7) of (2.5gm) of DESs (Reline) showed the best result.

Acknowledgements
We are grateful to the department of Chemical Industries, Institute of Technical, Mosul, for the facilities given to perform this work. Thanks are also to College of Science, University of Mosul and Al-Noor University College to support this research.
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