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Preparation and Efficiency of Environmentally Friendly Metal Working Fluid (Mwfs) from Chemical Modification of Waste Cooking Oil

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Abstract

To produce ecofriendly and proficient metal working fluids and also to decrease the impact of waste cooking oil in the environment, waste cooking oil was recycled in novel prepare. Waste cooking oil was glycolyzed utilizing polyethylene glycol 400, 600 and 1000 gm to allow the glycolyzed products (GWCO-400, GWCO-600 and GWCO-1000). The prepared additives were utilized as emulsifiers to form metal working fluid application in presence of cooking oil, castor oil, and Jatropha oil as environmentally friendly oils. The outcomes demonstrated great soundness of the prepared water-vegetable oils emulsions. The pH, specific gravity, kinematic viscosity at 40 ^{o}C, surface tension, and anticorrosion tests of the obtained MWFs gave acceptable results compared to several working fluids formulations.

Keywords: Waste cooking oil; glycolysis; vegetable oils; working fluids; anticorrosion.

1. Introduction

The machining industry utilizes enormous amounts of water and oils for dissipating the cutting device temperature, improving the surface completion of parts and expanding instrument life. In the current situation, the market for metalworking fluid is around 1100 million USD [1], and it is assessed to contact 1500 million USD by 2020. Perpetually, the cutting fluid will get defiled with use, should be arranged to the climate. It was apparent from the writing that cutting fluids involve 16.9% of machining cost [2]. The report by National Institute of Occupational Safety and Health [3] shows that inward breath of oil-based metalworking fluid vaporizers may aggravate the throat, nose, and lung and has been related with chronic bronchitis, asthma and worsening of previous respiratory issues. The cutting fluids are fundamentally base oils blended in water called as emulsions. The soundness of the emulsions is identified with the improvement of an electrical layer in the oil - water interface. Repulsive forces among particles of the similar charge evade their blend. The water in the emulsion will make erosion the metal and to dodge this, anticorrosive added substance sodium nitrate was utilized [4]. Other than stability, emulsions are inclined to bacterial assaults and the microbial growth, which may prompt erosion and helpless lubrication properties. The microbial growth is decreased by adding 0.15% biocides by weight [5]. In spite of the fact that these biocides are antimicrobial, they discharge formaldehyde and is cancer-causing to specialist's wellbeing [6].

The work done in sustainable metalworking fluid is significantly ordered into dry machining [7-9], high pressure cooling strategy [10, 11] air [12], vapour, gas coolant, cryogenic cooling [9, 13, 14], and minimum quality lubrication-MQL [15].

2. Experimental Techniques

2.1. Chemicals

Poly ethylene glycol (Mwt 600 g/mole) was analytical grade and supplied from Sigma Aldrich, Germany. Castor oil, Jatropha oil, and cooking oil

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were supplied from local market. Waste cooking oil (WCO) was a collection of waste products.

2.2. Instrumentation

FTIR Spectroscopic measurements were performed utilizing ATITM Mattson Infinity series, Bench top 961 controlled by Win First TM V2.01 software. Kinematic viscosity measurements were performed utilizing Analis p-121 viscosity bath, Belgium. pH measurements were performed utilizing InoLab, pH 720 WTW model, Germany. Copper strips were standard copper samples according to ASTM D 665.

2.3. Synthesis

2.3.1. Glycolysis of waste cooking oil (WCO)

Waste cooking oil (WCO) was glycolyzed by polyethylene glycol as a glycolyzing agent without using any catalyst consistent with the procedures of Ref [13]. Waste cooking oil (WCO) (50 g) and polyethylene glycol(٤٠٠-600-1000) (90 g) were charged in 500 mL one necked flask and heated. Temperature was raised gradually (5 ^{o}C per minute) and fixed at 250 ^{o}C for 3 h [14]. Then, the glycolyzed product was allowed to cool at room temperature and the medium was filtered in a stainless steel mesh with appropriate mesh diameter to take out the un-reactants. The obtained glycolyzed WCO was designated as GWCO 400, GWCO 600 and GWCO 1000.

2.3.2. Formulation of metal working fluids

The prepared additives (4 mL) were used as emulsifiers in the preparation of the metal working fluids in the following configuration: 90 mL distilled water, 5 mL of natural oil (Castor oil, Jatropha oil, and cooking oil), and 1 g of Tween-40 (as co-surfactant). The mixture was mixed in high speed mixer (5000 rpm) for 15 minutes at 25^{o}C.

2.4. Evaluation of Metal Working Fluids Additives

2.4.1. Emulsion Stability

It defines the stability of the metal working fluids preparations and their capability to be homogeneous during storage, carriage and application [15]. The metal working fluid preparations which formed using the presence of the synthesized additives were located in graduated cylinders at 25 ^{o}C and the look of oil layer in each cylinder was watched during 14 days in term of oil layer volume in mL. The emulsion stability (%) was calculated in percent according to the following equation:

$$\textbf{Emulsion stability } \% = \left(\mathbf{1} - \frac{\textbf{volume of oil separated}}{\textbf{total volume of oil in emulsion}}\right) \times \mathbf{100}$$

2.4.2. Kinematic Viscosity at 40 oC

It describes the viscosity of the metal working fluid preparation at 40 ^{o}C which is appropriate for metal working at low temperatures of bending and twisting which is appropriate for metal working at high temperatures of metal working and welding [16]. The measurements were performed using Ubbelohde suspended level viscometer with a capillary diameter of 0.3 mm for measurements at 40 ^{o}C,

2.4.3. Anticorrosion Test

The maintenance of the metal amid the handling in the presence of the metal working fluid formulations was tested by copper strip test according to the standard method [17]. A copper strip was immersed in the distinctive formed metal working fluids (300 mL) at 25 ^{o}C in three replicates for 24 h and the test strip is noticed for indications of erosion and the grade of this corrosion. The corrosion grade was considered in a scale from 0 to 10. No corrosion was 10 grade and completely corroded was 0 grade.

2.4.4. Specific Gravity

It defines the workability of the metal working fluid formulation during the handling of metal fabrics. The quantities were performed utilizing (specific gravity flask) of 25 mL. An empty flask was weighted accurately, and then it was filled by the metal working fluid preparation, and weighted. Test was repeated three times at 25 ^{o}C, and the average was careful [18]. The change in the weight was used to measure the specific gravities of the metal working fluids according to this equation:

$$\text{Sp. Gr.} = \frac{\text{weight of the filled flask} - \text{weight of the empty flask}}{\text{volume of the flask}}$$

2.4.5. Surface tension

It defines the surface spreading of the metal working fluids formulations on the metal surface in term of surface tension value. Surface tension data (γ) of the various formulations were measured by using Du-Noüy tensiometer (Krüss type K6) (Hamburg,

Germany) utilizing platinum ring detachment method. The tensiometer was calibrated by deionized water at 25 ºC. The surface tension measurements were taken after 10 min. of pouring the solution in the measuring cup to ensure the equilibrium [19].

2.4.6. pH values

It defines the acidity or alkalinity of the metal working fluids formulations and their inclination to cause erosion for the metal surface. The values of pH were reported using a pH meter for the different formulated metal working fluids at 25 ºC after prepare formulation.

2.4.7. DLS studies.

Is a technique in physics that can be used to determine the size distribution profile of small particles in suspension or polymers in solution .

2.4.8. GPC molecular weight

We measured molecular weight be waters 515/2410 Gel Permeation Chromatograph (GPC, Waters, America) and a Ultrahydrogel column calibrated with poly(ethylene glycol) standards and series 2410 refractive index detector. Mobile phase: water, sodium nitrate (0.10 M), Solvent: Water, sodium azide 0.05%, Flow rate: 1 mL/ min, Temperature: 25ºC.

3. Results and Discussion

3.1. Structure

The chemical structure of the waste cooking oil (WCO) showed the following absorption bands: weak absorption band appears at 3470 cm^{-1} corresponds to stretching of O-H group; 3008 cm^{-1} correspond to CH olefinic; 2854 and 2925 cm^{-1} correspond to CH_2 groups;1748 cm^{-1} corresponds to C=O; 1651 cm^{-1} corresponds to C=C; 1373 cm^{-1} corresponds to CH_3; 1163 cm^{-1} corresponds to C-O ether group and 721 cm^{-1} corresponds to CH_2 *Figure 1*.

FT-IR spectroscopy of GWCO-400, GWCO-600 and GWCO-1000 (*Figure 2a,b,C*) show the presence of band at 1651 cm^{-1} shifted to 1644 cm^{-1} and very clear because increasing C=C by poly ethylene glycol ; band at 3470 cm^{-1} shifted to 3372 cm^{-1} and very clear because increasing in OH group by poly ethylene glycol and band at 3008cm^{-1} not clear.

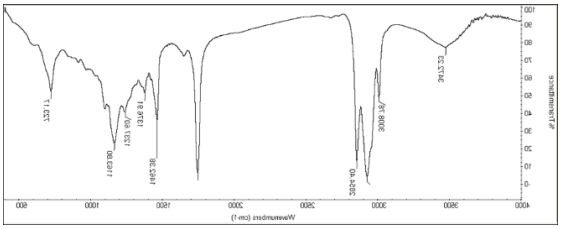
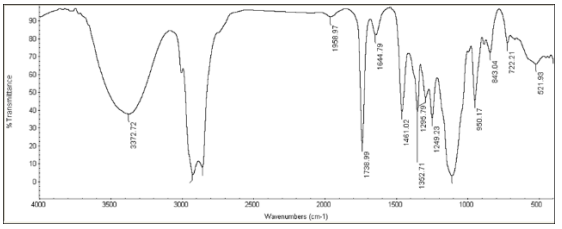
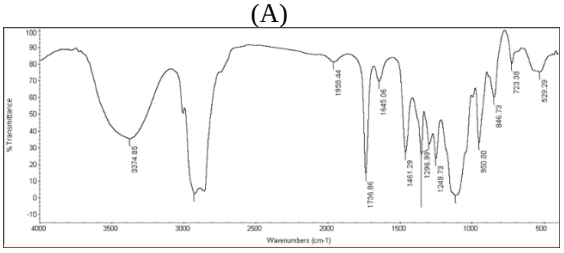


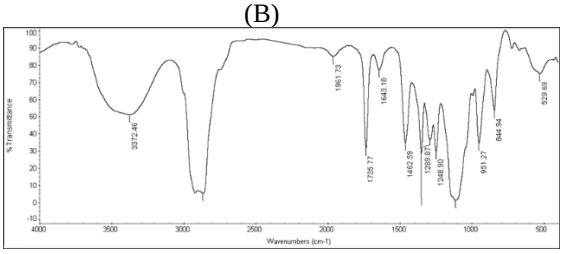
Figure 1: FT-IR spectrum of WCO.



(A)



(B)



(C)

Figure 2: (A) FT-IR spectrum of GWCO-400, (B) FT-IR spectrum of GWCO-600, (C) FT-IR spectrum of GWCO-1000.

3.2. Evaluation of the Metal Working Fluids Preparations

3.2.1. Corrosion Inhibition Properties

The capability to provide corrosion protection is significant for metal working fluids. The oil in water emulsions expressed in the presence of the created additives evaluated for corrosion creation on copper strips. ***Table 1*** signifies the results of the anticorrosion test before and after created additive added to the preparation after 1 and 10 days of immersion. The rust is formed on the metal surface during its dealing out due to its interaction by water and atmospheric oxygen. One role of metal working fluid is avoiding the rust formation on the metal surface during metal dispensation [20]. The origin of anticorrosion creation in the presence of the communicated metal working fluid is the presence of two active moieties in the

chemical structure of the produced additives. The first is the alkyl moieties of oleic, linoleic or fatty acid mix found from oil hydrolysis. Saturated and unsaturated fatty acids were reported as effective additives for corrosion inhibition in metal working fluids formulations [21]. Unsaturated fatty acids containing oleic acid, linoleic, recinoleic and maleic acids were combined in metal working fluid formulations as anticorrosion additives and presented excellent anticorrosion test results in presence copper and iron metals [22]. The second is the polyethylene glycol chains in the chemical structure of the prepared additives, which rises the adsorption of the additives on the metal surface. That defends the metal surface from the effect of corrosive compounds [23]. The anticorrosion test results recorded in ***Table 1*** show two performances. After one day immersion in the metal working fluid, the copper surface displayed no corrosion effect on the surface; 10 unit on anticorrosion scale. The results of anticorrosion after one day immersion show high protective tendency of the formed emulsion. After ten day immersion of copper strips in the prepared metal working fluids, the anticorrosion scale was ranged between 8 and 9. The results display high antirust effectiveness of the different formulations. The adapted preparations have hydroxyl and long chain alkyl chains, which may be in control for the rust inhibition [24]. These results are in good agreement with the results obtained for copper metal in contact with different partially hydrolyzed waste cooking oil, jatrova oil, and castor oil [25]. The obtained inhibition effectiveness was at the maximum at 8 days, and then the corrosion products start to form. In case of the prepared additives, the emulsions studied exposed excellent rust inhibition properties after 10 days. It can conclude that this metal working fluid has worthy capability to prevent the corrosion.

3.2.2. Kinematic viscosity

Viscosity is an important property with respect to fluid performance and maintenance. Lower viscosity fluids permit grit and dirt to settle out of postponement. Elimination of these impurities advances the quality of the fluid recirculating through the machining system. This can effect produce excellence, fluid life and machine shop output. Kinematic viscosity signifies the viscosity of the metal working fluid preparation used at the metal surface. Viscous metal working fluids are satisfactory in the machining procedures. The great viscosity of vegetable oils gives the metal working fluid an oily aspect and good lubricating properties. At sure viscosity, the increase will decrease the efficacy of the metal working fluids due to the loss of fluidity and consequently the lubricity power of the fluid reductions.

The kinematic viscosity of the metal working fluids preparations depend on two influences as can be understood from the data listed in ***Table 1***. The first is the type of oil used in making the metal working fluid preparation. Higher viscosity oil produces higher viscosity preparation. In case of preparations contain castor oil (as oil phase); the values of kinematic viscosities are ranging between 85 cSt and 155 cSt at 40 ^{o}C, which are the highest values. While in case of cooking oil and jatropha oil (as oil phase), the gotten viscosities are ranging between 86.8 cSt and the maximum at 117.6 cSt at 40 ^{o}C. That can be attributed to the relative low viscosities of rapeseed oil and coconut oil compared to castor oil. Increasing the temperature to 100 ^{o}C decreases the viscosities of the metal working fluids preparations considerably, ***Table 1***. The second factor is the molecular weight of poly ethylene glycol In the presence of PEG-600, the viscosities of the preparations were the maximum. While the preparations contain PEG-400, and PEG-1000 have lower viscosities.

Kinematic viscosities at 40 ^{o}C of sunflower oil, jatropha oil, and castor oil are: 41.55 cSt [26], 52.76 cSt [27], and 93.4 cSt [28], respectively. The kinematic viscosity of the formulated metalworking fluid contains castor oil was ranged between 86.8 - 92.4, while in the presence of cooking oil was 92.4-117.6, and 87.3-104.7 in the presence of jatropha oil. Comparing the kinematic viscosities of the tested metal working fluids containing different vegetable oils emulsified by partially hydrolyzed vegetable oils [28-30] showed comparatively high viscosity of the former than the later. That showed the high efficiency of the prepared metal working fluids in the presence the synthesized additives.

3.2.3. Emulsion stability

A metal working fluid preparation is simply an emulsion of oil and water. The constancy of that emulsion is a key phenomenon which determined the applicability of the metal working fluid in metal handling [31]. The emulsification power determines the stability of the metal working fluid after certain time. Decreasing the emulsion stability of the metal

working fluid leads to the separation of the oil and aqueous phases into two separate layers. Generally, the formulated metal working fluids with the synthesized additives showed stable emulsions up to 30 days, ***Table 1***. Several studies indicated that the emulsion stabilities of the metal working fluids are changed relying upon the emulsifiers utilized. Sulfonated vegetable oils as emulsifiers displayed 12 day stability [32]; while epoxidized soybean oil with organo-sulfur phosphorus demonstrated moderate emulsion stability within the presence of soybean oil at 18 days [33]. Synthesized compounds, S–[2–(acetamido)thiazol-l-yl]dialkyldithiocarbamate, added substances in rapeseed oil were assessed [34] and showed relatively high emulsion stability at 40 days.

Analyzing the data in ***Table 1*** revealed that the stability of formed emulsions depend mainly on the oil type and fatty acid residue linked to GWCO. In case of GWCO, the stabilities of the emulsions formed from castor oil and cooking oil were comparatively high compared to emulsion formed from water and jatropha oil. That can be attributed to the high percentage of oleic acid content in the chemical structure of the castor oil and cooking oil. The oleic acid abundance in jatropha oil is much lower than castor and cooking oils [21], [35]. Hence, the compatibility of the emulsifier with jatropha oil is very low. As a result, the obtained emulsion is highly unstable.

On the other side, the emulsifiers prepared from the fatty acid mixture hydrolyzed from the different oils showed very high stable emulsions for their oils (fatty acid mixture of cooking oil vs. emulsion contains cooking oil). GWCO-600 derivatives showed the lowest emulsification tendency towards the different oils. That may be attributed to two factors: the chemical structures of the different oils (low oleic acid content), and the low solubility of the emulsifiers in the aqueous phase. From the emulsification tendency measurements of the synthesized emulsifiers, it can be concluded that the emulsifiers of oils in metal working fluids are specific chemicals, and their stability depends on their compatibility with the used oil.

3.2.4. Surface tension

Metal working fluids are performing their lubricating action due to the distribution of oil between the metal surface and fabricating tools [34], [36]. The distribution of the metal working fluid on the metal surface depends on the contact between the liquid and the metal, i.e., surface or interfacial tension.

Decreasing the surface tension of the metal working fluid formulations increases their distribution on the surface. The surface tension values of the formulated metal working fluids by the synthesized additives as emulsifiers are ranged between 33 and 37 mN/m. The low surface tension values of the formulated metal working fluids are attributed to the surface activity of the synthesized additives [36]. The surface active characters of the synthesized additives were obtained from the hydrophobic and hydrophilic moieties in their molecules [37]. The hydrophobic character is owned to the presence of the fatty acids linked to their chemical structures. While, the nonionic chains of polyethylene glycols in the chemical structures of the various added substances are the hydrophilic parts [38]. The presence of the two characters increases the surface activity of the added substances and decreases their surface tension and interfacial tension to lower values [39]. The surface tension values (***Table 1***) are viewed moderate to low compared with several metal working fluids formulations containing: polysorbitan stearyl ester (42.5 mN/m), hexadecyl triethoxylate (39 mN/m), and monostearyl glycerol (32.5 mN/m) [20]. Commercial metal working fluids containing distinctive fatty acids provided comparatively higher surface tension values ranged between 39 and 58 mN/m [40].

3.2.5. pH values

Acidity or alkalinity of metal processing medium is a strong reason for metal corrosion. Reserving the medium at neutral pH protects the metal against corrosion (especially copper and aluminium) [35, 41]. The pH values of the prepared formulations are ranging between 5 and 7.0 after 7 days, ***Table 1***. These values don't change by time, indicating the chemical stability of the different formulations. The derivatives are esters formed between different fatty acids and glycolyzed polyurethane. Hydrolysis of the ester additives as metal working fluids formulations can occur. The risk of esters hydrolysis is found in alkaline medium (at higher pH values than 8) and also in slightly acidic medium (at lower pH values than 6).

Table 1: Tribological properties of the formulated metal working fluids in presence of the synthesized additives

Oil phase	Additive	Surface tension, mN/m	Specific gravity, g/mL	Viscosity @40 ºC, cSt	Emulsion stability, day	pH	Anticorrosion test *	
							1 day	10 day
Cooking oil	**GWCO 400**	38	1	95.2	30	7	10	9
	GWCO 600	38	1	117.6	30	7	10	9
	GWCO 1000	38	1	92.4	30	6	10	9
Castor oil	**GWCO 400**	38	1	120.4	30	7	10	9
	GWCO 600	38	1	123.2	30	7	10	9
	GWCO 1000	39	1	120.4	25	7	10	8
Jatrova oil	**GWCO 400**	38	1	86.8	28	6	10	9
	GWCO 600	40	1	92.4	15	6	10	9
	GWCO 1000	41	1	89.2	26	6	10	9

*Antirust test result after 1 day in absence of additives was 5; and it was 2 after 10 day under experiment condition.

3.2.6. GPC molecular weight

We can notice that molecular weights for formulations GWCO-400, GWCO-600, GWCO-1000 are 620, 820, 1200 respectively we can notice that by increase molecular weight of polyethylene glycol molecular weight of formulation increase *Figure 3*.

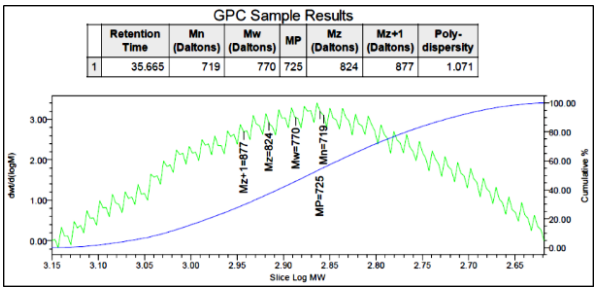
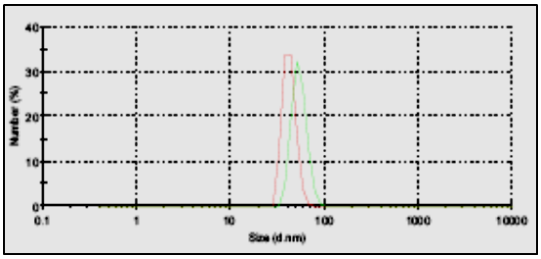


Figure 3: Molecular weight of GWCO-600

3.2.7. DLS studies

long of series of carbon were effect on particle size, we can notice that size of particles for formulations GWCO-400, GWCO-600, GWCO-1000 are ٥١,٨١, ٥٤,١٣, ٨٣,٤٤ respectively we can notice that by increase long chain of carbon in polyethylene glycol size of particle increase because the chain of PEG soluble in water and by increase long chain of carbon in PEG decrease repulsion between water and fatty acid so the size of particle of formulation increase *Figure 4*.



Z-Average (d.nm) :359. peak 1: size(d.nm) 269.1%number 0.4 width(d.nm) 58.48

Peak 2:size(d.nm) 54.13 %number 99.6 width(d.nm) 9.739

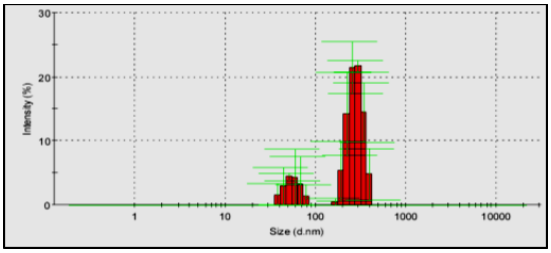


Figure 4: DLS of (GWCO-600MWt)

4. Conclusions

From the results of the study several concluding points can be extracted:

1. The synthesized additives have high emulsification power and produce stable oil in water emulsions, compared to the commercial and recently synthesized nonionic sorbitan, polyethylene glycol and glycerol based emulsifiers.
2. The anticorrosion property of the prepared emulsions is very high, and reached to 30 days, which is comparatively high efficiency.
3. The spreading power of the emulsions prepared by the synthesized additives is high compared to the nonionic additives.
4. The acidity of the emulsions prepared is in an acceptable range of 6 to 7.
5. The efficiencies of the formulations formed by the synthesized additives are comparatively higher than the formulations contained nonionic surfactants and modified vegetable oils.
6. The emulsifiers are specific for the oil used in metal working fluid formulation and can be prepared from the hydrolyzed fatty acids of the oil incorporated in the formulation.

5. Conflicts of interest

All authors have participated in writing this manuscript, this manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.

"There are no conflicts to declare".

6. Acknowledgments

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