Membrane technology for treating of waste nanofluids coolant: A review

By Amrifan Saladin Mohruni

Membrane Technology for Treating of Waste Nanofluids Coolant: A Review

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Abstract. The treatment of cutting fluids wastes concerns a big number of industries, especially from the machining operations to foster environmental sustainability. Discharging cutting fluids, waste through separation technique could protect the environment and also human health in general. Several methods for the separation emulsified oils or oily wastewater have been proposed as three common methods, namely chemical, physicochemical and mechanical and membrane technology application. Membranes are used into separate and concentrate the pollutants in oily wastewater through its perm-selectivity. Meanwhile, the desire to compensate for the shortcomings of the cutting fluid media in a metal cutting operation led to introduce the using of nanofluids (NFs) in the minimum quantity lubricant (MQL) technique. NFs are prepared based on nanofluids technology by dispersing nanoparticles (NPs) in liquids. These fluids have potentially played to enhance the performance of traditional heat transfer fluids. Few researchers have studied investigation of the physical-chemical, thermo-physical and heat transfer characteristics of NFs for heat transfer applications. The use of minimum quantity lubrication (MQL) technique by NFs application is developed in many metal cutting operations. MQL did not only serve as a better alternative to flood cooling during machining operation and also increases better-finished surface, reduces impact loads on the environment and fosters environmental sustainability. Waste coolant filtration from cutting tools using membrane was treated by the pretreated process, coagulation technique and membrane filtration. Nanomaterials are also applied to modify the membrane structure and morphology. Polyvinylidene fluoride (PVDF) is the better choice in coolant wastewater treatment due to its hydrophobicity. Using of polyamide nanofiltration membranes BM-20D and UF-PS-100-100, 000, it resulted in the increase of permeability of waste coolant filtration. Titanium dioxide is nanomaterials additive to modify the Nanopores of the surface membrane. Contact angle and average pore size were used in the investigation of the surface morphology of membranes. An adequate choice in modifying the membrane surface in waste coolant filtration may bring a promised alternative as a solution in waste coolant remediation.

INTRODUCTION

Membrane technology is the most promising filtration in water treatment process in the twenty-first Century. Membranes are used in various industrial processes and plants such as water purification, wastewater reclamation. The development of science and technology of membrane application is growing rapidly from the laboratory to

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industrial-scale application. One of the modern applications of the porous membrane in wastewater treatment is to remove emulsions of different sizes [1]. This method is conducted by using the ability of low pressure to force the dispersed phase to permeate through the membrane into a continuous phase in the form oil in water or water in oil solutions. This liquid waste is generated in a significant concentration in the machining process.

Coolants are an essential component of machining process as it cools the cutting zone, lubricates the tool-chip contact thereby reducing the friction and temperature generated. Meanwhile, the metal working industries saw the limitation of the use of conventional coolant and coolant strategies. Among the alternative ways of conventional coolant usage reduction, dry machining and minimum quality lubrication (MQL) technique are useful in the machining process to foster the sustainable environment. MQL in comparison with flood cooling and dry machining drastically minimises (1/300,000 times) the adverse effect on the environment, resulting in reduce of cutting force and usage of coolant [2]. However, the lubricating oil tends to evaporate as it struck the already heated cutting tool at high temperature. The need of thermal conductivity nanoparticles in cutting fluids is explored to eliminate or reduce the shortcomings of conventional coolants in MQL technique drastically.

Nanofluids (NFs) are new classes of fluids engineered by dispersing nanomaterials in base fluids that could be deionized water, esters or vegetable oils (e.g. Coconut oils) [3]. Nanomaterials are defined as the materials whose structural have dimensions in the range between 1 and 100 nanometers. In nanomaterials due to the increase of surface area to the volume, some physical and chemical properties such as thermal, electrical, mechanical, chemical, optical and magnetic property of the materials can be changed significantly. The nanomaterials exhibit different and unique properties as compared to the bulk materials with the same compositions [1]. NFs are the class of solid/liquid mixtures engineered by dispersing nanoparticles in conventional base liquids. Conventional nanoparticles could be metallic/intermetallic compounds, namely Ag, Cu, Ni, Fe ceramic compounds, namely oxides, sulphides, carbides, Al2O3, Fe2O3, TiO2, SiO2, ZnO2 are some nanostructured materials [2, 4]. Base liquids of NFs are a vegetable oil, coconut oil, gear oil, and pump oil. NFs were applied in different areas such as thermal application, fuel additives, lubricant, surface coating, environmental remediation, inkjet printing, biomedical, and petroleum industry. An example of the NFs thermal applications is a cooling system in different sectors, such as a metal cutting operation. Cooling is most potential scientific challenges in various industries for heat transfer applications [5]. NFs can be used in metal processing and could also be used as an effective coolant in data centres and electronics cooling systems, as shown in Figure 1 [1]. NFs have also applied in environmental remediation as an additive in membrane composition to produce nanofiltration membrane.

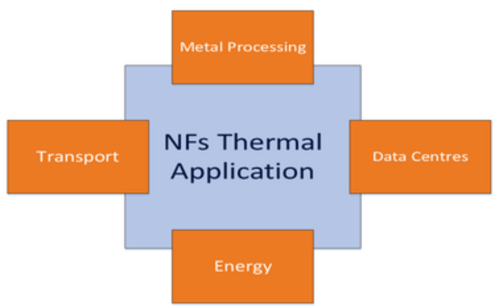

FIGURE 1. NFs thermal applications

Proper selection of coolants is of particular importance as it could affect the tool life, cutting forces, power consumption, machining accuracy, surface integrity, etc. [7]. Despite the significant effects of coolants in the machining process, the selection of the type and delivery system of the coolants are usually based on the recommendations of coolants suppliers and machine tool manufacturers. Substances used in machining for cooling and/or lubrication can be defined as cutting fluids, gas-based coolants/lubricants and solid lubricants. It has been used widely accepted characteristics of the coolants is their miscibility in water. Then, it has been used to categorise the coolants into water-soluble or non-water-soluble, also known as oil-based coolants [8].

Oil-based fluids are one of alternative coolant used in machining operations. They are classified into two basic categories such as naphthenic mineral oils and paraffinic mineral oils. Based on the limitation of mineral oils, some studies develop the use of vegetable oils as coolants in machining operations [8]. Moreover, vegetable oils are classified as nanofluids that potential to enhance the performance of conventional heat transfer fluids. Stability of NFs is one of the key features for any NFs system in each application, especially heat transfer application.

The study of the stability of NFs including the key factors which influence the stability as well as the techniques which can be used for the evaluation of the stability of NFs is necessary. Factors affecting the stability of NFs was showed in Figure 2, which influence the stability of NFs and based on that to achieve stable NFs, surface modifiers (such as surfactants), pH adjustment, NFs preparation method, mixing/homogenization as well as nanoparticles loading vital play role. It should be mentioned that each NFs system needs its particular dispersion method to stabilise the nanoparticles in base liquid to achieve stable suspension.

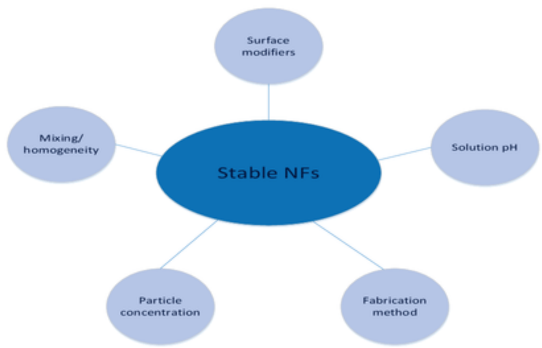

FIGURE 2. Factor Affecting Stability of NFs

MEMBRANE FILTRATION APPLICATION

Membrane filtration is the use of a particular porous material manufactured for the interception role in the physical removal of a certain way of the trapped particle size of contaminants. The difference in pressure driven membrane filtration is divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Waste oil characterises the membrane filtration according to the particle size, membrane molecule weight cut off (MWCO) has no phase change, a direct realisation of the oil-water separator; without pharmaceutical dosing, less pollution; low reprocessing costs, the filtration has less energy consumption; separation of water has low oil content. It needs to be modified the neat membrane to be more useful in the filtration process. Membranes will be amended by adding the nanoparticles to enhance the membrane performance.

Membrane Classification

MF and UF typically operate at low pressure, e.g. <6 bars, but NF and RO run at relatively high pressure, e.g. >8 bars. In the real filtration process, the MF and UF membranes approximately do not depend on the membrane pore size and actual solute sizes in rejecting molecules. This phenomenon caused by the cake layer formed on membrane surface acts as a dynamic membrane. However, the existence of this type of dynamic membranes has no influence when rejecting of the tiny molecules that have low molecular weight perhaps less than a few tens of thousands Dalton. In this case, the UF perform better than MF in rejecting the molecules. Another type of membranes such as NF and RO were effectively used in removing ions and trace organic molecules in the filtration of water. Due to the looser skin layer structure, NF membranes tend to pass monovalent ions (Li^+, Na^+, K^+, etc.), but not di- and trivalent ions (Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, etc.). Figure. 3 illustrates classification of membrane filtration as a function of molecular weight cut off and pore size.

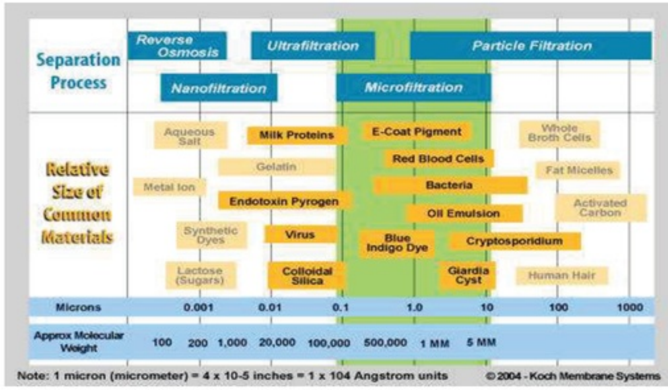

FIGURE 3. Classification of membrane filtration as a function of molecular weight cut off and pore size (Koch Membrane Systems).

Performance Evaluation of Various Membrane Materials for the Coolant Wastewater Treatment

The membrane filtration technology is characterised by waste coolant/waste oil according to the particle size membrane MWCO reasonable certainty. The process has no phase change, a direct realisation of oil-water separator without pharmaceutical dosing, so less pollution, reprocessing costs low and has less energy consumption. Li et al. (2006) applied a tubular ultrafiltration (UF) module equipped with polyvinylidene fluoride membranes modified by inorganic Nano-sized alumina particles to purify oily wastewater from an oil field. Results showed that added nanoparticles alumina improved membrane antifouling performance and flux recovery ratio of modified membranes achieved 100% washing with 1 wt. % of OP-10 surfactant solution (pH 10) [9]. Zhang et al. (2009) applied polysulfone (PSf) to treat oily wastewater. The results revealed that oil retention was 99.16% and oil concentration in the permeation was 0.67 mg/L, which met the requirement for discharge (<10 mg/L). This research has proven that developed composite membrane with adding nanomaterials are reasonably resistant to fouling and hence the modified PSf membranes are considered feasible in treating oily wastewater [10].

Abadi et al. (2011) prepared a tubular ceramic microfiltration (MF) (α-Al2O3) system for the treatment of typical oily wastewater [11]. The permeated was contained with oil and grease of 4 mg/L that met the National Discharge Standard and exhibited TOC removal efficiency to be higher than 95%. The results showed the best-recommended process condition by Trans Membrane Pressure (TMP) of 0.125 MPa, cross-flow velocity (CFV) of 2.25 m/s and temperature of 32.5 °C. Backwashing was used to remove oil droplets and particulates which blocked the membrane pores and could also prevent flux decline significantly. Mittal et al. (2011) employed nanomaterials ceramic-polymeric composite membrane from clay, kaolin and a few binding materials for treating oily wastewater to minimise the final cost of the composite membrane [11]. This condition showed that higher pressure and higher initial oil concentration resulted in higher flux decline. The maximum rejection was reached of 93% at 41 min for an initial oil concentration of 200 mg/L at 138 kPa.

Sarfaraz et al. (2012) investigated the possibility of nanoporous membrane powdered activated carbon (NPM-PAC) to treat the oily wastewater [13]. Results demonstrated neat NPM was ineffective in removing total suspended solids (TSS), chemical oxygen demand (COD) and total organic carbon (TOC). The COD and TOC removal were 62.2% and 75.1% respectively, and the value of flux was 78.7 L/m2h. In this experiment, the addition of PAC dosage in membrane solution decreases deposit layer with a high porosity on the membrane surface, which the flux increases up to 133.8 L/m2h and removal of COD and TOC were 78.1% and 90.4% respectively. Therefore, it can be concluded that NPM-PAC hybrid membrane system has the potential method to improve membrane fouling and permeation flux with a cross flow filtration system in the desalter plant. Salahi (2013) produced a sheet nanoporous Poly Acrylonitrile (PAN) membrane in pore size of 10 nm for treating oily wastewater. The results showed that nanoporous membrane is efficient for treating petroleum refinery wastewater in a desalter plant. TSS, oil and grease content, COD, BOD were increased to 100%, 44.4%, 99.9%, 80.3%, and 76.9%, respectively. Table 1 listed oily wastewater treatment by membrane filtration [13].

TABLE 1. Oily wastewater treatment by membrane filtration

Type of membrane	Results	References
Polyvinylidene fluoride membranes modified by inorganic nanosized alumina particles Ultrafiltration	Oil content is below 1 mg/L	x
Composite polysulfone (PSf)	Oil retention was 99.16%, and oil concentration in the permeation was 0.67 mg/L	Zhang et al. (2009)
Tubular ceramic microfiltration (MF) (α-Al2O3)	Oil and grease content of 4 mg/L and exhibited TOC removal efficiency was higher than 95%.	Abadi et al. (2011)
Hydrophilic ceramic-polymeric composite membrane	The maximum rejection was reached of 93% at 41 min for an initial oil concentration of 200 mg/L at 138 kPa.	Mittal et al. (2011)
NPM-PAC nanoporous membrane	COD and TOC removal were 78.1% and 90.4% respectively	Sarfaraz et al. (2012)
PAN nanoporous membrane	TSS, oil and grease content, COD, BOD were increased to 100%, 44.4%, 99.9%, 80.3%, and 76.9%, respectively	Salahi et al. (2013)

Effect of Nanoparticles (NPS) Additives on Membrane Morphology

Polyvinylidene fluoride (PVDF) is a widely used polymer for making porous membrane for oily wastewater treatment. PVDF is a crystalline phase polymer that provides the thermal stability and also an amorphous phase that is flexible towards membranes. PVDF is also unfluctuating with corrosive chemicals and organic compounds such as acids, alkaline, strong oxidant and halogen. Moreover, PVDF is a hydrophobic polymer while attacked by PVDF is un-fluctuated by the corrosive chemicals and organic such as acids, alkaline, strong oxidants and halogen. Moreover, PVDF is a hydrophobic polymer that potential in oily wastewater treatment based on membrane [14]. Composition effect of solvent, additive, and coagulation media was also investigated [15]. In general, large voids were formed by using water as a coagulant, while the voids were decreased by using alcohol and mixture of water and alcohol or water and solvent. The solvent effect on the structure of membrane was investigated by Yuliwati et al. (2010) [16]. The solvent of DMAc and DMF and also different nanoparticles composition as an additive in PVDF dope solution [16]. Fontananova et al. [5] studied the impact of nanoparticles of PVP and LiCl in casting solution on the formation of PVDF membrane. The membranes, which are fabricated using by rapid phase inversion rate method tends to form macro voids with finger-like structure; meanwhile, a slow phase inversion rate produces membranes with a sponge-like structure. Formation of the macro void can be terminated by LiCl at high concentration of 7.5%, whereas at low concentration of 2.5% LiCl enhances the permeate flux.

Among the mostly used inorganic nanoparticles, titanium dioxide (TiO2) is the best choice regarding its excellent performance like contact angle measurement, good chemical stability, antibacterial property in membrane fabrication for wastewater treatment [17]. Yang et al. concluded the morphology of cross-section changed from macro voids to sponge-like with increasing of TiO2 nanoparticles in membranes. The viscosity of dope solution also increases by adding the TiO2 nanoparticles [18]. Furthermore, Cao et al. investigated the addition of nanoparticles led to better hydrophilicity and permeation properties. The water contact angle was measured at 250C for drop ages 50-100 seconds about 70 – 850 [19]. Table 2 tabulated the values of contact angle and hydraulic permeability of PVDF membranes.

TABLE 2. Values of contact angle, hydraulic permeability and mean pore radii [19-21]

Membrane	Contact angle Θ	Lhi x 109 (m3/m2 Pa s)	rpm (nm)
PVDF/ Al_2O_3	45	n.a	n.a
PVDF/ $LiClO_4$/ TiO_2	40.04	n.a	n.a
PVDF/$LiClO_4$	80	n.a	50.0
PVDF/LiCl	82	n.a	22.5

SUMMARY

Study and develop modified membrane material with nanoparticles additives have been reviewed. It can be concluded that modified PVDF material by adding the nanoparticles offers many more advantages compared to the neat membrane in oily wastewater treatment, especially coolant wastewater filtration. Application of PVDF membrane in the metal industry for long-term performance could be an alternative solution regarding the purpose of nanoparticles in the membrane to minimise fouling and prolong the membrane lifetime that effects directly to enhancement fo the efficiency of the treatment process. Heterogeneity of coolant effluent has been reported by some researchers because it is made by nature and effect of fouling that was harder to control and forecast. The fouling phenomenon of the membrane is one of the drawbacks in membrane technology that cannot be prevented but can be minimised. It has been reported that hydrophilicity membranes are more advantages concerning fouling than hydrophobic membranes. Some researchers said the impact of pore-forming hydrophilic additives on membrane structure and performance could improve membrane permeability and reduce fouling. This condition distributed to develop a further study that needs to be conducted to select the additive nanomaterial for efficient machining processes.

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