CHAPTER 6

SUSTAINABILITY THROUGH THE DEVELOPMENT OF GREEN ALTERNATIVE LUBRICANTS IN THE MACHINING PROCESSES

Muhamad Azwar Azhari, Noordin Mohd Yusof,
Ani Idris, and Nor Hasrul Akhmal Ngadiman

6.1 INTRODUCTION

The depletion of petroleum reserves and the impact that petroleum-based oil lubricant waste imposes upon the environment has caused a shift in lubricant formulation from the commercially available petroleum-based products to a precursor that is renewable, biodegradeable and non-toxic vegetable oil. Prior studies have shown that vegetable oil is a suitable candidate to substitute mineral base oil as a light machinery lubricant (Sneha et al., 2019). The easily available canola oil, rapeseed oil, palm oil and olive oil down to the more exotic oil such as karanja oil, avocado oil, cottonseed oil and hazelnut oil were studied by various researchers as the concern upon the environment consistently grow. Vegetable oil is seen as a suitable substitute for a lubricant precursor, for the content of triglycerides which are glycerol and free fatty acids (Menon & Rajasekaran, 2023). These compounds facilitate the sliding motion between contacting surfaces resulting in increase of lubrication. While vegetable oil is seeming to be able to replace mineral oil as lubricant, neat vegetable oil is not capable to be used as a lubricant as the double bond between Carbon chains causes the oil to oxidise and decompose (Owuna, 2020). Neat vegetable oil as lubricant do not lubricate the contacting surfaces efficiently as it increases the coefficient of friction and wear between contacting surfaces. Let us look at brief on how oxidation of vegetable oil takes place when used as lubricant.

When vegetable oil is exposed to oxygen and heat, the chain will initially break forming free radicals. These free radicals those were formed during this reaction will further react with oxygen to form peroxyl redicals (ROO•). Following the initiation step is the propagation step where the peroxyl radicals formed will then react with the other carbon chain forming peroxide (ROOH). Further reaction through branching and termination processes causes the carbon molecules to eventually be longer than the original carbon chain (Azhari et al., 2014). The steps of the auto-oxidation process are detailed in Table 6.1.

Table 6.1 Oxidation steps of vegetable oil

Steps	**Equation**
Initiation	R-H → R• +H
	R• + O_2 → ROO•
Propagation	ROO• + R-H → ROOH + R•
	ROOH → RO• + OH•
Branching	RO• + R-H → ROH + R•
	OH• + R-H → H_2O + R•
Termination	R• + R• → R-R

To overcome this issue, various types of additives have been added to different types of oil as to increase the oxidation stability and enhance other tribological properties. To increase the oxidation stability of lubricant through reduction of oil decomposition, an anti-oxidant additive shall be added. This is indeed essential as to increase the life span of lubricant oil. Two different types of anti-oxidants namely primary anti-oxidants which are radical scavengers and secondary anti-oxidants or peroxide decomposers are normally used to reduce oxidation in lubricating oil. Primary anti-oxidants scavenged any free radicals (namely alkyl free radicals or alkyl peroxyl radicals) and donates Hydrogen atoms to eliminate the oxidation process. Secondary anti-oxidants on the other hand decompose any peroxide those were produced during oxidation process. With the decomposition of peroxide, branching and termination process will be interrupted causing the oxidation process to halt. Organo-metallic compounds consisting zinc and/or molybdenum and sulphur are usually added as anti-oxidizing agents in lubricant formulation. Lesser known anti-oxidants used include aromatic amine and hindered phenolic compounds.

Improvement of tribological properties of a lubricant is done through the addition of additives that reduces friction and wear which is anti-wear and friction modifier additives (Cyriac et al., 2022). These additives were incorporated in base oil to reduce the friction between contacting surfaces through the formation of a protective barrier that will result in a lower sheer stress that causes the coefficient of friction to reduce. As sufficient amount of additives was added, the tribo-film generated will also act as a sacrificial layer as the contacting surfaces slide between each other. The sacrificial tribo-film layer generated will provide a protective cushion that avoids direct contact which eventually mitigates wear between contacting surfaces. Sulphur containing compound, chlorine containing compound, phosphorous containing compound and organo-metallic compound are the general types of anti-wear additives usually added into base oil to increase the tribological properties. Some examples include molybdenum disulphide, triphenyl phosphorothionate, zinc dialkyldithiophosphate (ZDDP) and chlorinated fatty oils.

Various vegetable oil has been used as a precursor in developing a sustainable lubricant with the addition of zinc dialkyldithiophosphate and zinc diamyldithiocarbamate (ZDDC). zinc dialkyldithiophosphate was developed in the 1930s and since then ZDDP and ZDDC has been studied extensively and being added into various types of oil to increase the tribological properties (Huynh et al., 2021). This golden coloured