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Utilization of Bio-oil from Corncob Pyrolysis for Aromatic Extraction in Raw Lubricant Oil

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Abstract. Corncob is one of the biomass wastes which has abundant amount in Indonesia. Through pyrolysis, corncobs can be converted into bio-oil containing compounds such as furans and phenolics, which can be utilized as extractants of aromatics in raw lubricant oil. In high temperature, the aromatic content in engine lubricants can affect physical properties of the lubricants causing wearing on engine parts. The objective of the present research is to investigate effect of the weight ratio of extractant (solvent) to raw lubricant oil and the composition of aromatic in raw lubricant oil on the extent of aromatic extraction. The former work used extractants of bio-oil containing furans and phenolics, furfural and phenol for comparison, while the latter used extractant of bio-oil containing furans and phenolics. Pyrolysis has been done in a stirred tank reactor with a heating rate of 5°C/min and a maximum temperature of 500°C. Bio-oil from the pyrolysis contained many low molecular weight oxygenates dominated by carboxylic acids, which comprise 37% volume of bio-oil. Combined fractions of furans and phenolics have been isolated from bio-oil as bottom product from centrifuge and it comprises 5% weight of the original bio-oil obtained from pyrolysis of biomass. The bottom product to be used as aromatic extractant contained guaiacol (41.69%), phenol (27.29%), and furans (12.77%), with no carboxylic acid detected. The weight ratio of extractant to raw lubricant oil was varied 1:1, 2:1 and 3:1 with a constant initial weight composition of aromatics of 60%, and the initial weight composition of aromatics in raw lubricant oil was varied 30%, 45% and 60% with constant weight ratio of extractant to raw lubricant oil of 1:1. As the raw lubricant oil was a commercial lubricant and as an aromatic compound model was p-xylene. The aromatic extraction was performed at constant temperature of 40°C for 60 minutes. Aromatic extraction by furfural and bio-oil solvent shows that the greater solvent to lubricant ratio resulted in less raffinate yield, but more extraction intensity. Aromatic extraction by phenol shows that the greater solvent to lubricant ratio resulted in more raffinate yield and the extraction intensity reached minimum value as this ratio was 2:1. Aromatic extraction by bio-oil solvent shows that the more initial amount of aromatics in lubricant resulted in more raffinate yield, but less extraction intensity.

INTRODUCTION

Corn production in Indonesia increases consistently. In 1993 the production of corn was 6.4 million tons and tripled to 19.6 million tons in 2015. The increase of the corn production is proportional to the production of corn cobs waste. Corn cobs can be utilized to produce various compounds with various functional groups by pyrolysis method, such as furans and phenolics [4]. Furans and phenolic compounds can be used for many purposes, either directly used or as intermediate materials (raw materials for producing other compounds). One of the furan-derived compounds is furfural. The benefit of furfural and phenol is its utilisation as an extractant / solvent of aromatic compounds contained in lubricant oil, which is quite common [2].

Petroleum fraction to be processed into lubricant generally contains compounds such as cycloalkanes, isoalkanes, and aromatic compounds. Used oil is also proven to contain many aromatic compounds. The amount of aromatic compound content of the lubricant can affect some of the physical properties of the lubricant, including viscosity, response to additive, specific gravity, refractive index, flash point, pour point, and viscosity index (VI) of lubricants [2]. Apart from that, the presence of aromatics in lubricants due to high temperature condition during the use of lubricants in machines causes friction and wear effects on the lubricated surfaces [9]. To reduce aromatic

contents in a raw lubricant, extraction process is required using aromatic compounds such as furfural and phenol as extractants. Research has been done to prove that the higher the solvent to lubricant ratio, the more are the aromatics separated from the raw lubricant so that the viscosity decreases and the VI produced is greater [2]. Furfural and phenol may be obtained by biomass pyrolysis as part of products of furans and phenolics, respectively.

In biomass pyrolysis, there are two reaction steps, i.e. primary and secondary pyrolysis. Light molecular weight (LMW) oxygenates such as carboxylic acids, aldehydes, ketones, and alcohols may be produced by primary pyrolysis of biomass or by secondary pyrolysis via levoglucosan formation [6]. In addition, primary pyrolysis also forms char, noncondensable gases, furans and phenolics [3]. Bio-oil may be produced by fast or slow pyrolysis. Fast pyrolysis gives higher yield of bio-oil compared to slow pyrolysis, but bio-oil from fast pyrolysis has wider molecular weight range [8]. This may incur some problem when the separation of furans and phenolics from LMW oxygenates.

The objectives of the current research are to obtain furans and phenolic fraction of bio-oil from corn cob pyrolysis that can be utilized as an aromatic extractants or solvent in a raw lubricant, to obtain an optimum solvent to lubricant ratio leading to meeting the lubricant standards and lastly to determine the effect of the initial aromatic content in raw lubricant on effectivity in extracting aromatic.

METHODOLOGY

This research was conducted in a laboratory scale and consisted of three stages. The first stage was pyrolysis of corn cobs to produce bio-oil expectedly containing high composition of furans and phenolic compounds, the second stage is the isolation of furans and phenolic compounds from the bio-oil, and the third step is the utilization of an oil containing isolated furans and phenolic compounds as a solvent in the extraction of aromatic compounds in the raw lubricant.

The pyrolysis was carried out in a stirred tank reactor with a heating rate of 5°C/min, a maximum temperature of 500°C, a flow rate of N₂ 900 mL/min, and a stirring speed of 100 RPM. The isolation of the furans and phenolic fraction was performed by adding 50% NaOH until the pH of bio-oil became 6, then centrifuged at 3000 RPM for 30 min to separate the acetic acid-dominant phase and the furan and phenolic phase. The aromatic extraction was performed in a raw lubricant prepared using a commercial mineral lubricant added p-xylene as an aromatic compound model. The lubricant used in the present work for preparing a raw lubricant model was a commercial mineral lubricant of SAE 20W-50. This lubricant has a viscosity index of 130 and has a high resistance to oxidation and heat.

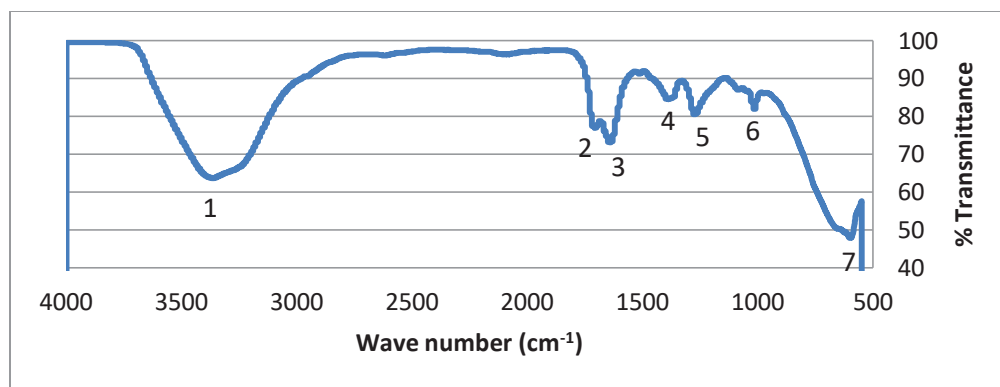
The aromatic extraction was performed in a two-neck pyrex flask, where the stirring and temperature was set with a magnetic stirrer. The solvent containing isolated furans and phenolic compounds was used as aromatic extractant with the solvent to lubricant ratio varied 1:1, 2:1, and 3:1 at constant extraction temperature of 40°C for 60 minutes. As a comparison, the same extraction was carried out using a commonly used solvent: pure furfural and pure phenol. The other variable variation was initial aromatic content in the raw lubricant varied 30%, 45%, and 60% at constant solvent to lubricant ratio of 1:1.

RESULTS AND DISCUSSION

Bio-oil Analysis

Corn cob pyrolysis produced 34.08% weight of bio-oil, 28.16% of char, and 37.76% of non-condensable gas. Nitrogen gas flow as a carrier gas brought the vapor product of pyrolysis out of the reactor to be condensed in a series of condensers. To maximize the yields of furans and phenolic compounds, the flow of nitrogen was set at 900 ml/min.

Bio-oil was then tested with FTIR to determine the possible functional groups in bio-oil. Based on Figure 1 below, it is seen that the functional groups produced from pyrolysis were dominated by alcohol, carbonyl, and aromatics. The alcohol group is indicated by O-H stretch (3550 - 3200 cm⁻¹) and O-H bend (1420 - 1330 cm⁻¹). Carbonyl group is indicated by the existence of C=O stretch (1780 - 1680 cm⁻¹). Aromatic groups are identified by aromatic C=C bend (1700 -1500 cm⁻¹) and aromatic C-H bend (860 - 680 cm⁻¹).



1. O-H Stretch
2. C=O Stretch
3. Aromatic C=C Bend
4. O-H Bend
5. C-O Stretch
6. C-C Bend
7. Aromatic C-H Bend

FIGURE 1. FTIR Analysis of Bio-oil Acquired from Biomass Pyrolysis

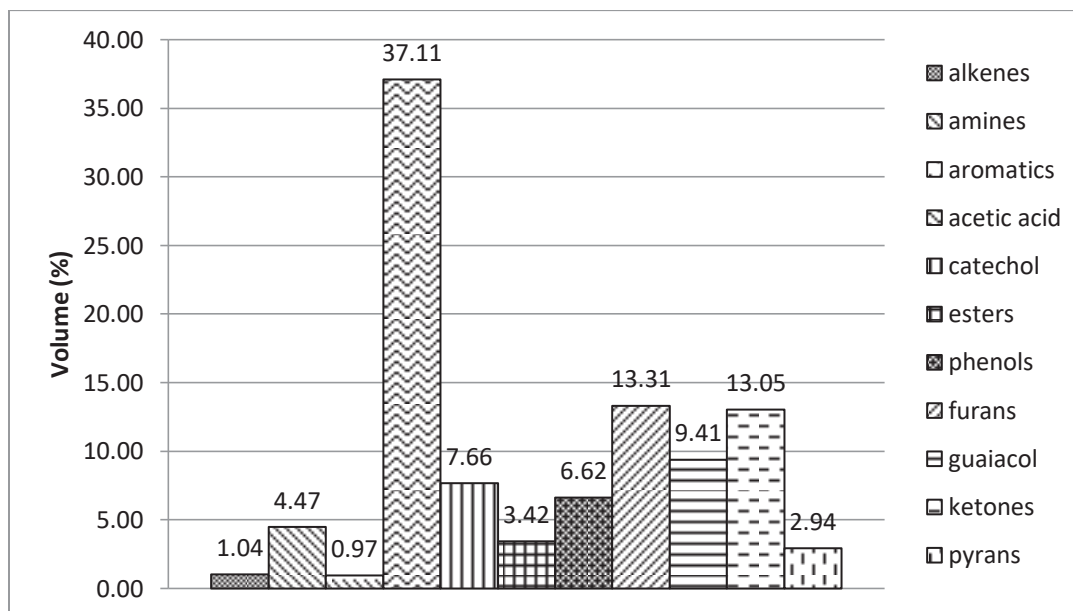


FIGURE 2. GC-MS Analysis of Bio-oil Acquired from Biomass Pyrolysis

FTIR test results are supported by GC-MS test to find out in more detail the content of compounds in the bio-oil. Figure 2 below shows the functional groups of the compounds detected in GC-MS. Figure 2 shows that compounds in the bio-oil in the order from the most to the least, i.e. acetic acid, phenolic compounds (combined phenol, catechol, guaiacol), furans (5-ring heterocyclic compounds), ketones, esters and pyrans. Acetic acid was mostly derived from O-acetyl group of hemicellulose pyrolysis, phenolic compounds originated from lignin pyrolysis, furans were mostly derived from cellulose pyrolysis, ketones and esters may have originated from hemicellulose and cellulose pyrolysis [1].

Isolation of Furans and Phenolic Compounds

Furans and phenolic compounds in the bio-oil were isolated by addition of 50% NaOH until pH of the bio-oil became 6, then put into centrifuge rotated at 3000 RPM for 30 min. After centrifugation, phase separation occurred

forming two layers in which the top layer was clear yellow as aqueous phase and the bottom layer was dark and highly viscous. The two phases resulting from separation is shown in the Figure 3.

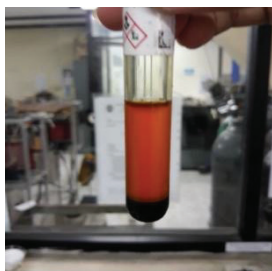


FIGURE 3. Upper and Bottom Layers of Bio-oil Generated after Acetic Acid Extraction on Bio-oil from Biomass Pyrolysis

The upper layer was aqueous phase, while the bottom layer by furans and phenolic compounds. The analysis of functional groups in bio-oil by GC-MS is shown in Figure 4. In the order of decreasing composition, bio-oil contained guaiacol (41.69%), phenol (27.29%), and furans (12.77%). Phenolics consisted of phenol, guaiacol and catechol. Figure 4 also proved that the bottom layer contained no acetic acid. From 30 g of polar phase of bio-oil obtained from biomass pyrolysis, 5 g of NaOH was added and 1.5 g of which (5%) was bottom layer containing furans and phenolic compounds. This yield was less than that acquired by Park et al [5] comprising 16% of their bottom layer. Such a small yield may have occurred due to too much NaOH added which can react with phenol and other compounds to form clear, aqueous solution in addition to the intended main reaction between NaOH and acetic acid.

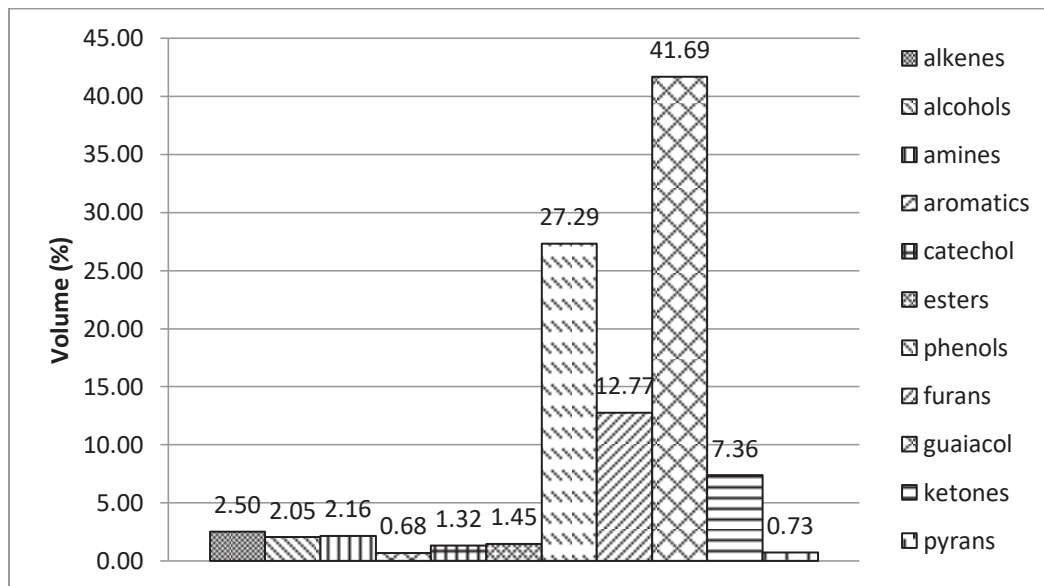


FIGURE 4. GC-MS Analysis of Bottom Layer Containing Furans and Phenolic Fraction

The absence of acetic acid in the upper layer indicates that NaOH may have been added excessively. The solubility degree of compounds in NaOH can be considered as the ease of the compounds forming their ions in NaOH solution. The value can be measured from its pKa, the dissociation constant of the acid. The pKa values of some compounds contained in bio-oil can be seen in Table 1.

TABLE 1. pKa Value of Some Compounds in Bio-oil

Compound	pKa
Acetic Acid	4.76
Phenols	9.98
Alcohols	> 15.5
Catechol	9.45
Guaiacol	9.98
Furfural	13.65
Ketones	18-21
Esters	25

The smaller pKa value indicates the corresponding compound is easier to dissociate into its ions. In bio-oil, acetic acid is a compound which has the smallest pKa value. Thus, when bio-oil is added with NaOH, acetic acid is the compound that most easily forms its ions and dissolves in NaOH solution.

Aromatic Extraction

Aromatic extraction was performed with two independent variables: solvent to lubricant weight ratio and initial aromatic content in lubricant. Lubricant in the present study was treated as if it was raw lubricant in commercial aromatic extraction. For the former work, aromatic extraction was performed using bio-oil containing furans and phenolics, pure furfural and pure phenol as solvents with the initial aromatic content in the lubricant of 60%. For the latter work, solvent used was only bio-oil containing furans and phenolics with the solvent to lubricant weight ratio of 1:1. Extraction took place in a pyrex flask at constant temperature of 40°C for 60 minutes.

Effect of Weight Ratio of Solvent to Lubricant on Aromatic Extraction

The result of the aromatic extraction with the solvent to lubricant ratio variation and its effect on the raffinate yield can be seen in the Figure 5. Raffinate yield is defined as the weight ratio of the remaining lubricant to the initial lubricant. Figure 5 indicates that there was a loss of initial lubricant as a result of extraction. Using furfural, which commonly used in commercial extraction, exhibits the lowest lubricant loss. Furfural and bio-oils show the same tendency, the increase in the weight ratio of solvent to lubricant caused larger loss of lubricant. This result is similar to that obtained Epelle et al [2] and Shakir & Qasim [7]. The tendency is quite different when the solvent used was phenol. The increasing volume of phenol mixed adversely displaced part of phenol into the lubricant. In another word, solubility of phenol into lubricant became higher as the volume of phenol mixed was increased. It seems that within the weight ratio of solvent to lubricant, phenol has reached its solubility saturation point and caused some phenol to dissolve in the lubricant. Phenol is a fairly polar compound. Its E_T^N (spectroscopic polarity index) value is 0.7. Compared to furans (E_T^N value of 0.164) and furfural (E_T^N value of 0.426), phenol has less ability to dissolve aromatics in lubricants, in which aromatics has $E_T^N < 0.1$, due to the less similarity in the polarity index.

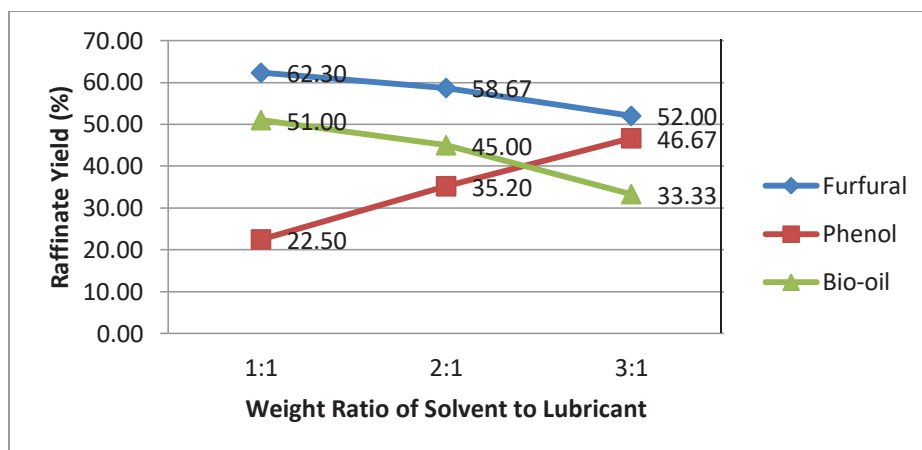


FIGURE 5. Effect of Solvent to Lubricant Ratio on Raffinate Yield. Three types of solvents used were furfural, phenol and bio-oil containing furans and phenolic compounds

Figure 6 presents the extraction intensity by different solvents at varied weight ratio of solvent to lubricant. The extraction intensity is defined as the weight ratio of (initial aromatics in lubricant - remaining aromatics in lubricant) to initial aromatics in lubricant. It can be seen from Figure 6 that furfural presented highest extraction intensity. Phenol performed different intensities at different weight ratio of solvent to lubricant. It seems that solubility of phenol in lubricant decreased as the content of phenol in the lubricant was small.

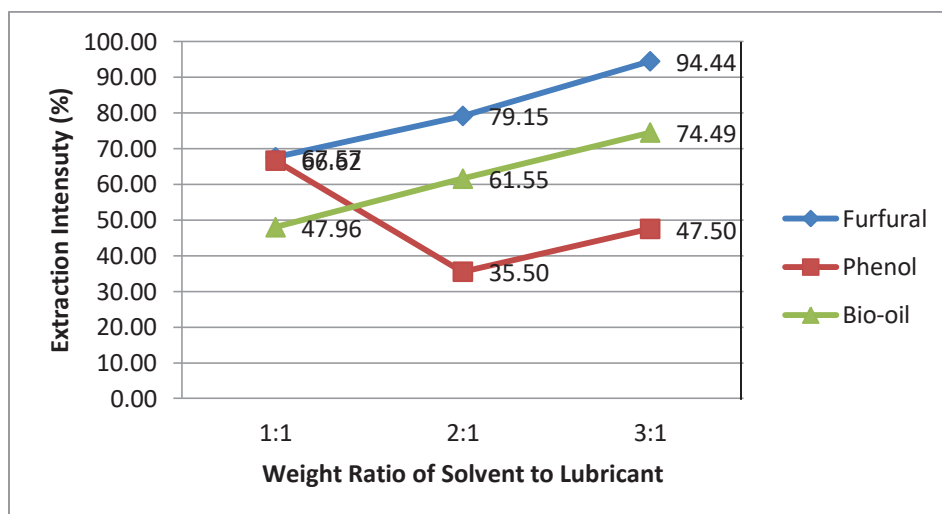


FIGURE 6. Effect of Solvent to Lubricant Ratio on Extraction Intensity. Three types of solvents used were furfural, phenol and bio-oil containing furans and phenolic compounds

Figure 6 shows that with furfural and bio-oil as solvents, the larger amount of solvent used, the higher was the aromatic extracted by solvent. Similar results were also obtained in researches conducted by Epelle [2] and Shakir & Qasim [7] where increasing solvent added to lubricant increases the viscosity index (VI) of lubricants which indicates less aromatic content in the lubricant. However, with phenol as a solvent, optimal result of extraction intensity was at the ratio of solvent to lubricant of 1:1. The addition of phenol exceeding a certain ratio caused phenol to surpass its saturation point and decrease the effectivity of dissolving aromatic compounds.

Effect of Initial Aromatic Content on Aromatic Extraction

The next step was to vary the initial amount of aromatics in the lubricant using the isolated furan and phenolic fractions as the solvent. Figure 7 describes raffinate yield defined as the weight ratio of the remaining lubricant to

the initial lubricant. The figure shows higher initial aromatic content in lubricant reduced the volume of lubricant but the reduction was much higher than the addition of aromatic to the lubricant. It seems that some fraction of lubricant was easily solved in the solvent when the aromatic content in the lubricant was high.

Figure 8 describes effect of the initial aromatic contents in lubricant on ratio of the non-extracted aromatics retained by lubricant to the initial aromatic content in lubricant. It can be observed that less initial content of aromatics in the lubricant resulted in less remaining aromatics in the lubricant and consequently more extraction intensity defined as the weight ratio of (initial aromatics in lubricant - remaining aromatics in lubricant) to initial aromatics in lubricant. The intensity for the initial aromatic amount in lubricant of 60% was 47.96%, the initial aromatic amount of 45% was 55.71%, and initial aromatic amount of 30% was 69.52%. Therefore, the higher initial aromatic content in lubricant would reduce the capability of solvent to extract aromatics.

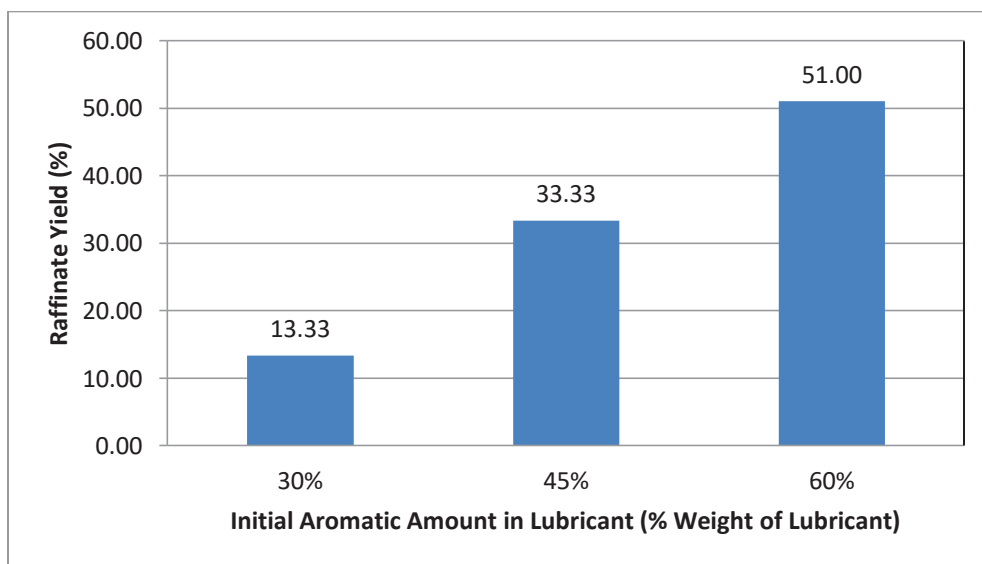


FIGURE 7. Effect of Initial Aromatic Number in Lubricant on Raffinate Yield.

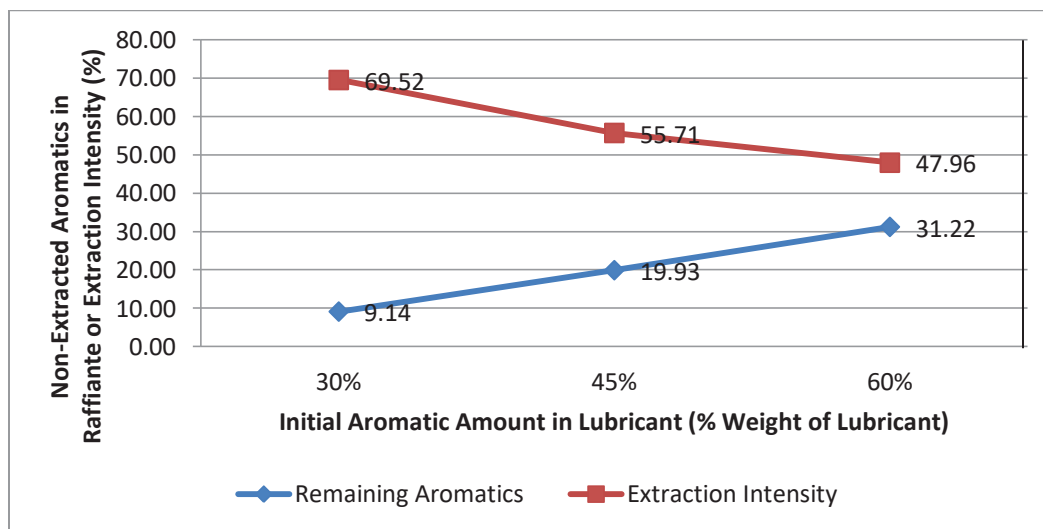


FIGURE 8. Effect of Initial Number of Aromatic in Lubricant on Remaining Aromatics and on Extraction Intensity

CONCLUSIONS

From the present study, some conclusions are drawn as follows

- Fractions of furans and phenolic compounds to be used as aromatic extractant has been isolated from bio-oil as bottom product from centrifuge and it comprises 5% weight of the original bio-oil obtained from pyrolysis of biomass. The bottom product contained guaiacol (41.69%), phenol (27.29%), and furans (12.77%), with no carboxylic acid detected.
- Aromatic extraction by furfural and bio-oil solvent shows that the greater solvent to lubricant ratio resulted in less raffinate yield, but more extraction intensity.
- Aromatic extraction by phenol shows that the greater solvent to lubricant ratio resulted in more raffinate yield. However, extraction intensity reached minimum value as this ratio was 2:1.
- Aromatic extraction by bio-oil solvent shows that the more initial amount of aromatics in lubricant resulted in more raffinate yield, but less extraction intensity.

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