BIOETHANOL PRODUCTION FROM SAGO PALM WASTE AS AN ALTERNATIVE FUEL FOR AUTOMOTIVE ENGINES

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I dedicate this thesis to my beloved parents, brother, sister and parent-in-laws.

Last but not least, to my beloved daughter and wife.
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ABSTRACT

The increasing demands of petroleum fuels, together with the environmental pollution issues, have motivated the efforts on discovering new alternative fuels. Bioethanol produced from biomass is considered as one of the important alternatives for petroleum fuels. In Sarawak, wastes from sago factories are currently causing serious environment problems. These wastes can be used as favourable feedstock for bioethanol production. The purpose of this research is to produce bioethanol from sago palm waste, and study the effects of bioethanol on corrosion of materials, and performance and emissions of petrol engine. First, bioethanol was produced from sago pith waste (SPW) using microwave hydrothermal hydrolysis accelerated by CO₂ (MHH) and microwave assisted acid hydrolysis (MAH). Bioethanol was also produced from sago bark waste (SBW) using microwave aided acid treatment and enzymatic hydrolysis (MAEH). Second, effect of bioethanol and gasoline blends on corrosion of materials was studied using static immersion test. Furthermore, corrosion of materials in biodiesel–diesel–ethanol (BDE) fuel blends was also studied. Finally, the effect of bioethanol on performance and emissions of petrol engine was studied. A maximum of 15.6 g and 30.8 g ethanol per 100 g dry SPW was produced using MHH and MAH, respectively. In addition, a maximum of 30.67 g ethanol was produced from 100 g dry SBW using MAEH. Corrosion of materials and degradation of fuel properties were 2.4 times higher in higher ethanol blends (above E25) compared to lower ethanol blends (up to E25). Corrosion and degradation of materials in BDE fuel blends was 1.7 times higher than petro-diesel. Petrol engine results showed that use of sago waste bioethanol (E25) significantly increased the engine power, torque, brake thermal efficiency, and mean effective pressure by about 4.5%, 4.3%, 9% and 4.2% compared to gasoline (E0), respectively. Emissions results showed a significant reduction in CO, NOₓ and HC emissions by about 42%, 7% and 5.2%, respectively for E25 compared to E0. This study acclaims that sago bioethanol is a feasible alternative to reduce the dependence on fossil fuels for the automotive industry.
ABSTRAK

Permintaan yang semakin meningkat untuk bahan api petroleum, bersama-sama dengan isu-isu pencemaran alam sekitar, telah mendorong usaha mencari bahan api alternatif baru. Bioetanol yang dihasilkan daripada biojisi dianggap sebagai salah satu alternatif penting untuk bahan api petroleum. Di Sarawak, sisa daripada kilang-kilang sagu kini mengakibatkan masalah alam sekitar yang serius. Bahan buangan ini boleh digunakan sebagai bahan mentah yang baik untuk pengeluaran bioetanol. Tujuan kajian ini adalah untuk menghasilkan bioetanol daripada sisa pokok sagu, dan mengkaji kesan bioetanol kepada kakisan bahan-bahan, dan prestasi dan pelepasan enjin petrol. Pertama, bioetanol dihasilkan daripada sisa empulur sagu (SPW) menggunakan ketuhar gelombang mikro hidrotermal hidrolisis dipercepatkan oleh CO₂ (MHH) dan ketuhar gelombang mikro dibantu asid hidrolisis (MAH). Bioetanol juga dihasilkan daripada sisa kulit (SBW) menggunakan ketuhar gelombang mikro dibantu rawatan asid dan hidrolisis enzim (MAEH). Kedua, kesan bioetanol dan petrol campuran ke atas kakisan bahan dikaji menggunakan ujian rendaman statik. Tambah lagi, kakisan bahan-bahan dalam biodiesel-diesel-etanol (BDE) campuran bahan api juga telah dikaji. Akhir sekali, kesan bioetanol ke atas prestasi dan pelepasan enjin petrol telah dikaji. Setiap 100 g SPW kering menghasilkan sebanyak 15.6 g dan 30.8 g maksimum etanol menggunakan MHH dan MAH masing-masing. Di samping itu, 100 g SBW kering menghasilkan 30.67 g maksimum etanol menggunakan MAEH. Kakisan bahan dan degradasi bahan api adalah 2.4 kali tinggi dalam campuran etanol tinggi (melebihi E25) berbandingkan kepada campuran etanol rendah (sehingga E25). Kakisan dan degradasi bahan-bahan dalam campuran bahan api BDE adalah 1.7 kali lebih tinggi daripada petro-diesel. Keputusan enjin Petrol menunjukkan bahawa penggunaan bioetanol hampas sagu (E25) memberi peningkatan ketara untuk kuasa enjin, dayakilas, kecekapan brek haba dan tekanan berkesan min, masing-masing sebanyak kira-kira 4.5%, 4.3%, 9% dan 4.2% berbanding petrol (E0). Keputusan emisi menunjukkan pengurangan ketara dalam emisi CO, NOₓ dan HC dalam kira-kira 42%, 7% dan 5.2% masing-masing untuk E25 berbanding dengan E0. Kajian ini menunjukkan bahan api bioetanol sagu adalah alternatif yang boleh dilaksanakan untuk mengurangkan pergantungan kepada bahan api fosil bagi industri automotif.
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<th>Description</th>
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<tr>
<td>1C</td>
<td>Single Cylinder</td>
</tr>
<tr>
<td>4C</td>
<td>Four Cylinders</td>
</tr>
<tr>
<td>4S</td>
<td>Four Strokes</td>
</tr>
<tr>
<td>AC</td>
<td>Air Cooled</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>B0</td>
<td>100% Diesel</td>
</tr>
<tr>
<td>B100</td>
<td>100% Biodiesel</td>
</tr>
<tr>
<td>B20D70E10</td>
<td>20% Biodiesel, 70% Diesel &amp; 10% Ethanol</td>
</tr>
<tr>
<td>B20D75E5</td>
<td>20% Biodiesel, 75% Diesel &amp; 5% Ethanol</td>
</tr>
<tr>
<td>B50</td>
<td>50% Biodiesel &amp; 50% Diesel</td>
</tr>
<tr>
<td>BDE</td>
<td>Biodiesel–Diesel–Ethanol or Bioethanol</td>
</tr>
<tr>
<td>BMEP</td>
<td>Brake Mean Effective Pressure</td>
</tr>
<tr>
<td>BP</td>
<td>Brake Power</td>
</tr>
<tr>
<td>BSFC</td>
<td>Brake Specific Fuel Consumption</td>
</tr>
<tr>
<td>BSHC</td>
<td>Brake Specific Heat Consumption</td>
</tr>
<tr>
<td>BTE</td>
<td>Brake Thermal Efficiency</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon Monoxide</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon Dioxide</td>
</tr>
<tr>
<td>CR</td>
<td>Compression Ratio</td>
</tr>
<tr>
<td>CV</td>
<td>Calorific Value</td>
</tr>
<tr>
<td>DE</td>
<td>Diesel–Ethanol or Bioethanol</td>
</tr>
<tr>
<td>DMC</td>
<td>Direct Microbial Conversion</td>
</tr>
<tr>
<td>DMF</td>
<td>Bio-Dimethyl Furan</td>
</tr>
<tr>
<td>DOHC</td>
<td>Double Overhead Camshaft</td>
</tr>
<tr>
<td>DVVT</td>
<td>Dynamic Variable Valve Timing</td>
</tr>
<tr>
<td>E0</td>
<td>0% Ethanol &amp; 100% Gasoline</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>E100</td>
<td>100% Ethanol &amp; 0% Gasoline</td>
</tr>
<tr>
<td>E25</td>
<td>25% Bioethanol &amp; 75% Gasoline</td>
</tr>
<tr>
<td>E50</td>
<td>50% Bioethanol &amp; 50% Gasoline</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersion Spectroscopy</td>
</tr>
<tr>
<td>EFI</td>
<td>Electronic Fuel Injection</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>EN</td>
<td>European Standard</td>
</tr>
<tr>
<td>ET</td>
<td>Engine Torque</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>FC</td>
<td>Fuel Consumption</td>
</tr>
<tr>
<td>FFV</td>
<td>Flexi Fuel Vehicle</td>
</tr>
<tr>
<td>FI</td>
<td>Fuel Injection</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse Gas</td>
</tr>
<tr>
<td>HC</td>
<td>unburned Hydrocarbon</td>
</tr>
<tr>
<td>HE or Eh</td>
<td>Hydrous Ethanol</td>
</tr>
<tr>
<td>HMF</td>
<td>Hydroxymethyl Furfural</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Pressure Liquid Chromatography</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>ITE</td>
<td>Indicated Thermal Efficiency</td>
</tr>
<tr>
<td>LHV</td>
<td>Lower Heating Value</td>
</tr>
<tr>
<td>MOA</td>
<td>Multi Element Analyser</td>
</tr>
<tr>
<td>MPFI</td>
<td>Multi-Port Fuel Injection</td>
</tr>
<tr>
<td>MS</td>
<td>Mild Steel</td>
</tr>
<tr>
<td>NBR</td>
<td>Nitrile Butadiene Rubber</td>
</tr>
<tr>
<td>NOx</td>
<td>Oxides of Nitrogen</td>
</tr>
<tr>
<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
</tr>
<tr>
<td>OM</td>
<td>Optical Microscope</td>
</tr>
<tr>
<td>PFI</td>
<td>Port Fuel Injection</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>RE</td>
<td>Renewable Energy</td>
</tr>
<tr>
<td>SBW</td>
<td>Sago Bark Waste</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SHF</td>
<td>Separate Hydrolysis and Fermentation</td>
</tr>
<tr>
<td>SI</td>
<td>Spark Ignition</td>
</tr>
<tr>
<td>SLC</td>
<td>Starchy Lignocellulosic</td>
</tr>
<tr>
<td>SOHC</td>
<td>Single Overhead Camshaft</td>
</tr>
<tr>
<td>SPORL</td>
<td>Sulfite Pretreatment Top Overcome Recalcitrance</td>
</tr>
<tr>
<td>SPW</td>
<td>Sago Pith Waste</td>
</tr>
<tr>
<td>SSF</td>
<td>Simultaneous Saccharification and Fermentation</td>
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<tr>
<td>TAN</td>
<td>Total Acid Number</td>
</tr>
<tr>
<td>VE</td>
<td>Volumetric Efficiency</td>
</tr>
<tr>
<td>WC</td>
<td>Water Cooled</td>
</tr>
<tr>
<td>WOT</td>
<td>Wide Open Throttle</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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LIST OF SYMBOLS

\( A \) - Surface area
\( \text{Abs.} \) - Absorbance
\( \rho \) - Density
\( l \) - Length
\( t \) - Time
\( W \) - Weight
\( N \) - Speed
\( \phi \) - Equivalent air-fuel ratio
\( \lambda \) - Relative air-fuel ratio
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CHAPTER 1

INTRODUCTION

1.1 Research Background

Worldwide increment in population growth rate, economic interdependencies between nations and the rapid developments in industries and automotive society have created several impeding issues around the world. These issues comprises of, but not limited to: uncompensated demands of petroleum based fuels that causes increasing fuel prices; environmental pollution problems; climate changes; energy crisis; and waste management. There is now global insistence to manage the above listed issues.

One of the promising solutions to address the above listed issues is renewable energy (RE) technology. RE sources, such as solar, wind, biomass, hydro, nuclear, geothermal, and tidal are most commonly utilized in different tropical location for power generation. RE sources have number of benefits, such as being sustainable having environmental and economic benefits; and pricing flexibility. However, the main drawbacks of most of the RE sources are reliability of supply due to unpredictable weathers, high capital cost and large land requirement. However, the biomass energy, which is among the RE family, can overcome the above mentioned drawbacks. There are many environmental benefits of using biomass energy as described below (IEA Bioenergy, 2005):
• reduced the reliance on limited natural resources
• reduced greenhouse gas (GHG) emission through fossil fuel replacement
• reduced landfill waste
• enhanced biodiversity
• protection of ground water supplies
• reduced dry land salinity and erosion

Currently, about 10 to 15% of world energy demand is supplied by bioenergy in developed countries, and the same is up to 3% in developing countries (Hosseini and Wahid, 2014). Figure 1.1 shows the share of biomass in world total primary energy supply. Most of the RE sources are utilized for electrical power generation globally. However, the global automotive and industry sectors are completely dependent on petroleum-based fuels as main energy source, which cannot be easily met by RE sources such as solar and wind other than bioenergy.

![Figure 1.1](image)

**Figure 1.1** Share of biomass in world total primary energy supply (IEA, 2014)

Presently, petroleum-based fuels are obtained from limited reserves, so there is a greater anxiety about the shortage of petroleum fuels due to finite reserves; moreover, environmental pollutions problem have been emphasized around the
world in recent days. Similar to the global situation, Malaysian automotive society is also more dependent on petroleum based fuels. The transportation sector of Malaysia has been the largest consumer of petroleum fuels and the largest contributor of GHG emission accounting more than 40% of the total GHG emission (Abdul-Manan et al., 2014). Thus, it is of urgency to find a suitable alternative fuels for automotive engines. The most preferred choice for replacing petroleum-based fuels as the main energy in automotive sector is biofuels (Demirbas, 2011).

Biofuels are produced from biomass and bioenergy crops through different conversion process, which are generally thermochemical or biochemical. Biofuels have gained progressive importance as alternative fuels for automotive engines. Biofuels have shared 10% in the world primary energy supply of $1.56 \times 10^{11}$ MWh by fuels in the year 2012 (IEA, 2014). Biofuels are classified based on the production technologies, namely, first, second, third and fourth generation biofuels (Demirbas, 2011). Table 1.1 shows the classification of biofuels based on different feedstock.

<table>
<thead>
<tr>
<th>Generation</th>
<th>Feedstock</th>
<th>Biofuels examples</th>
</tr>
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<tr>
<td>First Generation</td>
<td>Sugar, starch grains, vegetable oils and animal fats</td>
<td>Bio-alcohols such as ethanol, propanol and butanol, vegetable oils, biodiesel, green diesel, bio-syngas and biogas</td>
</tr>
<tr>
<td>Second Generation</td>
<td>Non-food crops, agriculture residues, woody biomass and municipal solid wastes</td>
<td>Bio-alcohols such as bioethanol and methanol, bio-oil, bio-dimethyl Furan (DMF), bio-hydrogen, bio-char and bio-Fischer–Tropsch diesel</td>
</tr>
<tr>
<td>Third Generation</td>
<td>Algae based</td>
<td>Vegetable oils, biodiesel and bioethanol, methanol, butanol</td>
</tr>
<tr>
<td>Fourth Generation</td>
<td>Vegetable oils and biodiesels</td>
<td>Bio-gasoline and jet fuel</td>
</tr>
</tbody>
</table>

First generation biofuels are mainly produced from the food based feedstock, such as sugar, starch, vegetable oils and animal fats. Second generation biofuels are produced from the feedstock, such as non-food crops, agricultural residues, wood and municipal solid wastes. Algae based biofuel production is named as third generation biofuels. Among the various classifications of biofuels, liquid biofuels,
namely, biodiesel and bioethanol offer promising alternatives for petroleum based fuels in automotive engines. Biodiesel is produced from vegetable oils or animal fats through transesterification process, and bioethanol is produced from biomass and bioenergy crops using biochemical conversion. Table 1.2 shows the processes of converting biomass into biofuels and corresponding energy services.

**Table 1.2: Conversion of biomass into biofuels (IEA Bioenergy, 2005)**

<table>
<thead>
<tr>
<th>Biomass resources</th>
<th>Processes</th>
<th>Biofuels</th>
<th>Energy services</th>
</tr>
</thead>
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<tr>
<td>Agriculture and forestry residues</td>
<td>Densification</td>
<td>Wood pellets</td>
<td>Heat</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Briquettes</td>
<td>Electricity</td>
</tr>
<tr>
<td>Energy crops:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass, sugar, oil</td>
<td>Combustion</td>
<td>Char/charcoal</td>
<td>Heat</td>
</tr>
<tr>
<td></td>
<td>Gasification</td>
<td>Fuel gas</td>
<td>Electricity</td>
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<tr>
<td></td>
<td>Pyrolysis</td>
<td>Bio-oil</td>
<td>Electricity</td>
</tr>
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<td></td>
<td>Esterification</td>
<td>Biodiesel</td>
<td>Transportation</td>
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<td>Fermentation</td>
<td>Bioethanol</td>
<td>Transportation</td>
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<td>Biomass processing wastes</td>
<td>Digestion</td>
<td>Biogas</td>
<td></td>
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<tr>
<td></td>
<td>Hydrolysis/fermentation</td>
<td>Biogas</td>
<td>Transportation</td>
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<tr>
<td>Municipal solid wastes</td>
<td>Digestion</td>
<td>Refuse-derived</td>
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<tr>
<td></td>
<td>Combustion</td>
<td>fuels (RDF)</td>
<td>Heat</td>
</tr>
<tr>
<td></td>
<td>Gasification</td>
<td>Biogas</td>
<td>Electricity</td>
</tr>
</tbody>
</table>

1.2 **Bioethanol as Alternative Fuel**

Bioethanol (ethanol, fuel ethanol, ethyl alcohol, grain alcohol, EtOH or CH$_3$-CH$_2$-OH) is one of the liquid biofuel, which is considered as a clean, renewable and green combustible fuel, alternative to petroleum fuels in internal combustion engines. The ethanol fuel has the properties of higher octane number, higher flammability limit, similar or lower flame speeds, and higher heats of vaporization than gasoline fuel (as in Table 1.3). These fuel properties allow for a higher compression ratio, shorter burn time and leaner burn engine, which leads to better performance over gasoline in internal combustion engines (Balat and Balat, 2009). The higher octane helps to run the vehicles more smooth, and keeps the vehicle’s fuel system clean for optimal performance (Kumar *et al.*, 2010).
Table 1.3: Fuel properties of ethanol and gasoline (Kumar et al., 2010)

<table>
<thead>
<tr>
<th>Property</th>
<th>Ethanol</th>
<th>Gasoline</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C₂H₅OH</td>
<td>C₃ to C₁₂</td>
</tr>
<tr>
<td>Specific gravity at 15.55 °C</td>
<td>0.79</td>
<td>0.72-0.75</td>
</tr>
<tr>
<td>Distillation temperature (°C)</td>
<td>78.4</td>
<td>32-210</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>Kinematic viscosity (mm²/s)</td>
<td>1.5</td>
<td>0.6</td>
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<tr>
<td>Reid vapour pressure at 37.8 °C (kPa)</td>
<td>17</td>
<td>35-60</td>
</tr>
<tr>
<td>Octane number</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) Research</td>
<td>111</td>
<td>91-100</td>
</tr>
<tr>
<td>(ii) Motor</td>
<td>92</td>
<td>82-92</td>
</tr>
<tr>
<td>Oxygen content (wt.%)</td>
<td>34.7</td>
<td>0</td>
</tr>
<tr>
<td>Stoichiometric air/fuel ratio (w/w)</td>
<td>8.97</td>
<td>14.6</td>
</tr>
<tr>
<td>Net heat of combustion (MJ/kg)</td>
<td>27</td>
<td>43.5</td>
</tr>
<tr>
<td>Heat of vaporization (kJ/kg)</td>
<td>900</td>
<td>400</td>
</tr>
<tr>
<td>Water solubility</td>
<td>∞</td>
<td>0</td>
</tr>
<tr>
<td>Vapour flammability limit (vol.%)</td>
<td>3.5-15</td>
<td>0.6-8</td>
</tr>
<tr>
<td>Maximum flame speed (m/s)</td>
<td>0.33</td>
<td>0.40</td>
</tr>
<tr>
<td>Flame temperature at 101.325 kPa (°C)</td>
<td>478</td>
<td>392</td>
</tr>
<tr>
<td>Color</td>
<td>Colorless</td>
<td>Colorless to light amber glass</td>
</tr>
</tbody>
</table>

The anti-knock characteristics of ethanol allow for a high compression ratio, and therefore, produce higher engine power output. In addition, higher heat of vaporization of ethanol and faster flame speed permit for increased fuel conversion efficiency compared to gasoline (Costa and Sodre, 2011). Ethanol acts as oxygenate in gasoline engines, elevating its oxygen content, allowing a best oxidation of hydrocarbon, reducing the amount of aromatic compounds and carbon monoxide released to atmosphere (Balat et al., 2008).

Globally, bioethanol production reached 24.6 billion gallons in 2014, up from 22.4 billion gallons in 2011. Bioethanol presently accounts for more than 95% of the global biofuel production, with the majority coming from first generation food based feedstock, such as sugarcane, corn, wheat and cassava (Lichts, 2015). Due to the ethical concern about the food being used as fuel raw material, researches have re-
directed their work on the second generation lignocellulosic feedstock (Balat and Balat, 2009).

Extensive research has been carried out on bioethanol production from lignocellulosic biomass in the past two decades. Rice straw, wheat straw, corn straw, and sugarcane and sorghum bagasse are the major agricultural wastes which are suitable for large scale bioethanol production in terms of quantity of biomass available. Moreover, the starchy lignocellulosic biomasses, such as waste from starch processing and potato food factories, beverage and brewery factories are promising feedstock for bioethanol production in the tropical locations. A short process chart for bioethanol production from lignocellulosic feedstock is shown in Figure 1.2.

![Figure 1.2 Ethanol fermentation from biomass](image)

The second generation of bioethanol fuel production from lignocellulosic biomass involves four different steps, such as pretreatment, hydrolysis, fermentation and ethanol recovery (as in Figure 1.2). Different pretreatments, such as physical, chemical, physico-chemical and biological have been studied in the past decade to alter structural characteristics of lignocellulosic biomass. Hydrolysis is an essential step to produce fermentable sugars which are then fermented into ethanol by microbial biocatalyst.
1.3 Research Problem Statement

Bioethanol fuel has the potential to replace petroleum fuels in internal combustion engines. However, the cost of bioethanol production (0.97 USD/litre) is high compared to petroleum-based fossil fuels (0.22 USD/litre) (Banerjee et al., 2010; Macrelli et al., 2012). Currently, large scale bioethanol production is mainly based on sugar containing raw materials (e.g. sugar cane) and starch grains (e.g. corn, wheat and cassava), which is not appropriate due to their feed value. The lignocellulosic biomass, such as agriculture waste, woody biomass, algae, and municipal solid waste is not only a sustainable feedstock, as it incurs low cost and is abundantly available (Limayem and Ricke, 2012).

Although lignocellulosic biomass is sustainable and abundant; the bioethanol fuel production from lignocellulosic biomass is not commercialized in many countries including Malaysia. The main obstacles in bioethanol production are high production cost and energy requirements. The conversion of biomass into bioethanol using energy efficient, economic and faster technique is the greatest concern for commercial bioethanol production. Currently, acid and enzymatic hydrolysis is widely employed to breakdown the starch, cellulose and hemicellulose of biomass into fermentable sugar. These existing approaches tend to be slow, expensive and of high dilutions that give poor yields of glucose (Fan et al., 2013).

In Malaysia, the availability of lignocellulosic biomass, such as waste from wood industry, agriculture residues, oil palm waste and sago palm waste is abundant. The sago palm wastes, namely, sago pith waste, sago bark waste and sago effluent are the starchy lignocellulosic by-product generated from *Metroxylon sagu* (sago palm) after extraction of starch. Sago bark, which is peelings from initial process, is generated in sago starch processing factories. It is estimated that about 5 to 15 tons of sago bark waste and about 50 to 110 tons of sago pith waste are produced daily from starch processing factories in Sarawak, Malaysia, which are currently washed off into the nearby stream together with waste water (Awg-Adeni et al., 2010). This can cause serious environmental problems in Sarawak, Malaysia.
In addition to the above problems in bioethanol production, material compatibility of bioethanol fuels in automotive engines is another issue, for which the engineers and manufactures are working to find a suitable solution. The addition of bioethanol to gasoline in petrol engines normally creates corrosion in fuel system materials. In petrol engines, fuel gets in contact with various parts contributing to corrosion. The blends of diesel and ethanol could be used in existing diesel engines without engine modification. In addition, the biodiesel–diesel–ethanol (BDE) blend represents an important alternative fuel for diesel engines; however, changes in the fuel composition and the introduction of new alternative fuel often results corrosion in fuel system metals, and degradation in fuel system elastomers and polymers.

Most of the spark ignition (SI) engine studies discovered a significant improvement in engine performance and emission reductions, such as carbon monoxide (CO) and unburned hydrocarbon (HC) for ethanol fuel compared to gasoline. However, carbon dioxide (CO$_2$) and oxides of nitrogen (NO$_x$) emissions were not significant (increased or decreased), and moreover, the brake specific fuel consumption (BSFC) also increased or decreased due to low calorific value of bioethanol fuel (27 MJ/kg) compared to gasoline (43.5 MJ/kg). There are contradictory results attained for CO$_2$ and NO$_x$ emission and BSFC (Masum et al., 2013), motivating for further investigations using lignocellulosic bioethanol, such as sago bioethanol.
1.4 Hypothesis of Research Study

Currently, acid and enzyme hydrolysis are generally employed to breakdown the starch, cellulose and hemicellulose of sago pith waste into fermentable sugar, however, little information only available in bioethanol production from sago pith waste using economic, environmental friendly and energy efficient method. Further experimentation required for sago pith waste to produce bioethanol using alternative hydrolysis. Hydrothermal hydrolysis offers an alternative way to hydrolyze starchy and cellulosic biomass into fermentable sugars. Bioethanol fuel production from sago pith waste using microwave assisted hydrothermal hydrolysis and microwave hydrothermal hydrolysis accelerated by CO$_2$ is required to be further experimented.

The acid hydrolysis aided with microwave irradiation offers an economical and energy efficient alternative method for bioethanol production from sago pith waste. The microwave assisted acid hydrolysis was widely used to produce glucose but with no emphasis on energy consumption to produce fermentable sugars. Moreover, a low concentration of acid (< 0.5 mol/L) was commonly used with long irradiation time (5 min to 30 min) to achieve maximum fermentable sugars. However, no information on the microwave assisted acid hydrolysis (both H$_2$SO$_4$ and HCl with ≥ 0.5 mol/L) for sago pith waste with an aim to develop energy efficient approach. In addition, microwave aided acid treatment followed with enzyme hydrolysis was used for bioethanol production from sorghum bagasse, wheat straw, and rape straw. However, no research is found on bioethanol production from sago bark waste using microwave aided acid treatment, which necessitates further investigation.

The corrosion behavior of metals in ethanol and gasoline blends was studied through electrochemical properties. However, little information is available on change of bioethanol fuel properties after exposure to metals and the corrosive nature of bioethanol fuel for metallic materials. In addition, the effect of sago waste bioethanol on corrosion and degradation of materials requires further investigation.
The corrosion behavior of materials (metals, polymers and elastomers) in different biodiesel, such as palm oil, rapeseed oil and sunflower oil was widely studied. Literatures show a gap that no study has reported on corrosion and degradation behavior of materials in biodiesel–diesel–ethanol (BDE) fuel blend. Moreover, none of the study investigated the change of BDE fuel properties after exposure to materials, and the corrosive nature of BDE fuels. Further experimentation is required to analyze the corrosive behavior of BDE fuel blend on engine fuel system materials.

Investigations on the effect of ethanol and gasoline on performance and emissions of SI engine were carried out in past decade. Hydrous ethanol was found to be suitable to reduce NO\textsubscript{x} and CO\textsubscript{2} emissions compared to anhydrous ethanol. Hydrous ethanol reduces the NO\textsubscript{x} and CO\textsubscript{2} emission, however, engine performance decreased. Thus, further experimentation is required for achieving significant reduction in NO\textsubscript{x} and CO\textsubscript{2} emissions, without affecting the engine performance. Literatures show a gap that the effect of sago waste ethanol on the performance and emissions of petrol engine need to be further investigated.
1.5 Objectives

The main objectives of this study are:

a) To produce bioethanol fuel from sago palm wastes using economic and energy efficient approach.

b) To evaluate the corrosion of fuel system materials in bioethanol and gasoline fuel blends.

c) To examine the compatibility of fuel system materials in biodiesel–diesel–ethanol (BDE) fuel blends.

d) To assess the effect of sago bioethanol fuel on performance and emissions of petrol engine.
1.6 **Scope of the Research Study**

The scope of this research is to achieve the objectives described below:

a) Bioethanol fuel was produced from sago pith waste (SPW) using microwave hydrothermal hydrolysis accelerated with CO\(_2\) (MHH) and without CO\(_2\). MHH was carried out for different microwave power rating (550, 700 and 900 W) and heating time (1, 2, 3 and 5 min).

b) Bioethanol fuel was also produced from SPW using microwave acid hydrolysis (MAH) using both H\(_2\)SO\(_4\) and HCl (0.5, 1.0 and 1.5 mol/L concentration only used to avoid decomposition of sugar). MAH was carried out for different microwave power (550, 700 and 900 W) and heating time (1, 2 and 3 min).

c) Bioethanol was produced from sago bark waste (SBW) using microwave aided acid pretreatment followed with enzymatic hydrolysis (MAEH) and fermentation. MAEH was carried for different microwave power (700, 900 and 1100 W), heating time (30 s, 1, 2 and 3 min), and biomass liquid loading (10, 20, 30, 40 and 50%).

d) Corrosive behaviors of bioethanol fuel (E10, E25, E50 and E85) and gasoline (E0) on metals (mild steel, copper and aluminum) were examined at room temperature (25 to 30 °C). Corrosion immersion testing was carried for 700 and 1400 h.

e) Corrosive behaviors of biodiesel–diesel–ethanol (BDE) blends (B20D75E5 and B20D70E10) on metals (mild steel, copper and aluminum) were studied at room temperature and 60 °C.

f) The impact of B20D75E5 fuel on degradation of elastomer, namely nitrile rubber (NBR) and polymer, namely polytetrafluoroethylene (PTFE) at 50 °C was studied.

g) The performance and emission characteristics of a 1.3 litre 4-stroke 4-cylinder petrol engine using three different fuel blends, such as E0 (100%...
gasoline), E25 (25% sago waste ethanol and 75% gasoline) and E25C (25% commercial anhydrous ethanol and 75% gasoline) were studied.

h) The properties of fuel blends (E0, E25 and E25C) were determined according to the American Society for Testing and Materials standards (ASTM D1298, ASTM D2699 & ASTM D240).

1.7 Significance of the Research

The importance of this study is to implement the economic and energy saving technology to produce bioethanol commercially in Malaysia, from the resources available locally within the country. The use of bioethanol fuel in transportation sector save significant amount of fossil fuels and reduce greenhouse gas emission in Malaysia. This research developed a novel technique (MHH) to produce bioethanol fuel from sago pith waste, which is suitable for any kind of starchy lignocellulosic biomass. Moreover, this research developed an economic, environmental friendly and energy efficient methods to produce bioethanol fuel from sago palm waste (pith and bark waste). An alternative waste management for sago factories in Malaysia to convert all the sago waste into a renewable fuel is also proposed in this research. Another importance of this research is to identify the suitable materials to make engine fuel system parts that can perform effectively with alternative fuels such as bioethanol. Investigation of corrosion behavior of materials in bioethanol fuel proposes proper materials to manufacture engine fuel system parts. Sago waste bioethanol produced in this research is suitable for petrol engine compared to gasoline for better engine performance and low engine out emissions.
1.8 Structure of the Thesis

This thesis reports the results of the research work carried out by the author during the years 2012 – 2015. The research focused on bioethanol fuel production from sago palm waste as an alternative fuel for automotive engines including material compatibility, and engine performance and emissions. The outline of the thesis is as follows:

In Chapter 1, the background of the research along with the importance of bioenergy and biofuels are discussed in the beginning. Then, the research problem is pointed out towards the essentials of bioethanol fuel production, and its effects on engine materials, engine performance and emissions. The hypothesis of the research is discussed through the literatures. Then, the objectives of this thesis are reported, followed with the scope and significance of this research. Finally, the structure of the thesis is presented in the end of the chapter.

In Chapter 2, a detailed literature review is presented about the existing bioethanol production technologies including the comprehensive review of various pretreatment techniques, hydrolysis and fermentation methods. In addition, types of lignocellulosic biomass, existing bioethanol production techniques from various starchy lignocellulosic biomasses, and its potential ethanol yields are reported. The importance of sago palm waste as a potential substrate for bioethanol production in Malaysia is also discussed. Moreover, existing studies in bioethanol production from sago palm waste is described. In addition, existing studies in corrosion behavior of metals in ethanol and gasoline blends are presented. Furthermore, existing studies in the corrosion behavior of various biodiesel and diesel blends are also discussed. Finally, a comprehensive review on effects of ethanol blended gasoline on SI engine performance and emission characteristics are described.

In Chapter 3, materials and experimental methodology utilized for bioethanol production from sago pith waste (SPW) and sago palm waste (SBW) are described (Sections 3.1 to 3.3). The materials and experimental methodology utilized to study
the corrosion of fuel system metals in bioethanol and gasoline blends are described in Section 3.4, additionally, the materials and experiments used to study the compatibility of automotive fuel system materials in biodiesel-diesel-ethanol (BDE) blend is presented in Section 3.5. Finally, the engine setup and experimental procedure used to investigate the effect of bioethanol fuel blend on performance and emissions of petrol engine are described in Section 3.6.

Chapter 4 describes the results and discussion of different methods (MHH, MAH and MAEH) used for bioethanol production from sago pith waste (Section 4.1 and 4.2) and sago bark waste (Section 4.3). Results and discussion for the methods used in the Sections 3.4 about the corrosion of metals in bioethanol and gasoline blends is described in Sections 4.4. In addition, results and discussion for the methods used in Section 3.5 about the compatibility of materials in in biodiesel-diesel-ethanol (BDE) blend are presented in Sections 4.5 and 4.6. Finally, the results and discussion for engine study is presented in Sections 4.7 and 4.8.

Chapter 5 provides the conclusions and findings of the thesis, highlighting the most important findings of each section. The suggestions for the future work are also provided at the end of the thesis.
REFERENCES


