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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background of Study**

Automotive industries have been developed in every second with advanced technologies. There are very much specialization in this industries including engine design, chassis, body, wiring, control system, lubricant etc. For example in fuel mixing system, most of cars in the early of its existence until 90's are using carburetor as medium to transfer an air-fuel mixture into combustion chamber. However, this technology has been replaced with injection system which resulting in betterment of car performance. In second case, the earlier cars have very kinked wiring system and most of the control panel is based on the manual-operated-system. This 'out-dated' technology was successfully replaced by microchip where less wiring is required and most of the control system can be automatically operated.

Same to fuel technology where the latest researches have proved that ethanol blends may replace gasoline as engine fuel. E10 is currently applied as commercial fuel in some Europe countries while E85 is lesser and still under researches. These fuels are also known as oxygenated fuels which has higher Rating Octane Number (RON) that might result in better combustion. Thus, emission rate is reduced significantly and also can helps to minimize the air pollution crisis.

However, there will be some affect in engine material due to this change especially for established vehicles. This report is purposely to know on the effect of the fuels when it is being used as engine fuel.

## **1.2 Problem Statement**

Emission from the current vehicles is increasing from time to time. This is due to the incomplete combustion of the gasoline fuel inside the internal combustion engine. In order to reduce the emission, ethanol-blend has been introduced. However, one of the ethanol's properties which are significantly more conductive than gasoline may increase electrochemical action. These different characteristics may result in a corresponding increase in degrading effects of ethanol fuel on materials in the fuel line. Exposure of metallic parts to high-percentage ethanol fuel blends may result in degradation in the form of corrosion of metals, metal platings, or surface treatments, stress cracking, embrittlement, or fatigue.

### **1.3 Objective of Study**

Objective of this study is to determine the feasibility of the blends fuel by analyzes its characteristic and behavior towards engine components' materials. Secondly is to experimentally study on the effects of the ethanol-gasoline blends fuel especially E10 and E85 to the material of fuel delivery system.

### **1.4 Scope of Study**

The scopes of this project can be divided into two which are first; determine the properties of the ethanol-gasoline blends through the established researches and to conduct an immersion testing to know the effect of E10 and E85 to the engine components material. The components are taken from fuel delivery system of used Honda Accord 2.0 (1996) which is fuel rail, pressure regulator and fuel injector.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Ethanol–Gasoline Blends Properties

The quality of the ethanol added to gasoline is important. The industry standard for ethanol is ASTM D 4806 Standard [1] Specification for Denatured Fuel Ethanol for Blending with Gasoline for Use as Automotive Spark Ignition Engine Fuel.

**Table 1: ASTM 4806 standard for ethanol fuels**

Property	Specification	ASTM Test Method
Ethanol volume %, min	92.1	D 5501
Methanol, volume % max	0.5	
Solvent-washed gum, mg/100 ml max	5.0	D 381
Water content, volume %, max	1.0	E 203
Denaturant content, volume %, min	1.96	
volume %, max	4.76	
Inorganic Chloride content, mass ppm (mg/L) max	40	D 512
Copper content, mg/kg, max	0.1	D1688
Acidity (as acetic acid CH <sub>3</sub> COOH), mass percent (mg/L), max	0.007	D1613
pHe	6.5-9.0	D 6423
Appearance	visibly free of suspended or precipitated contaminants	



It was also known as an octane enhancer since it improved the anti-knock performance of gasoline. In this decade, when many state governments prohibited the use of the predominant oxygenate, MTBE, ethanol then became the oxygenate of choice. Several states also have required ethanol use in winter as a way to reduce carbon monoxide emissions. Based on the research made by Dr. Ranajit (Ron) Sahu, consultant of Environmental and Energy Issues from United States (US), some of the changes in fuel properties [2] due to the addition of ethanol to gasoline include:

- Change in octane number
- Change in fuel volatility
- Change in the energy density
- Change due to the oxygen content
- Effect on water solubility and phase separation

These property changes can affect performance, emissions, or both. Ethanol also may affect the fuel's compatibility with various materials, which means it can affect the product's durability.

### **2.1.1 Change in Octane Number**

In general, addition of ethanol up to a certain amount improves gasoline's octane number due to its excellent anti-knock properties. Engines specifically designed to use high octane fuels, such as high performance engines, may use higher compression ratios or increase charge air compression to increase power output.

### 2.1.2 Change in Fuel Volatility

A fuel's ability to vaporize is referred to as its volatility. It is represented by several measurements, including vapor pressure, vapor-liquid ratio and the amount vaporized at different temperatures (distillation). The vapor pressure of the fuel, which is very important from both an emissions and performance standpoint, may be the property most familiar to the public. Typically, refiners optimize and maintain vapor pressure in a given range for performance, business, and regulatory purposes. If the vapor pressure of the fuel is too low, that may cause problems in starting engines in cold temperatures; if it is too high, it may cause vapor lock at high temperatures. In either case, the driver or operator will experience performance problems.

High vapor pressure and the presence of ethanol also increase evaporative emissions. The vapor pressure of ethanol is lower than that of gasoline. However, the addition of ethanol to gasoline, especially at lower concentrations, can actually increase the vapor pressure of the mixture to greater than that of gasoline. It depends on the amount of ethanol added and the composition of the base gasoline. For blends using a base gasoline with a vapor pressure of 0.07 bar or 9 psi, the vapor pressure increase reaches a maximum around E5, and then slowly starts to come down with further increase in ethanol concentration [3].

Thus, the effect of ethanol-gasoline blends on engine performance is that gasoline does not ignite as a liquid, only as a vapor. There must be sufficient fuel vapor present inside the combustion chamber to initiate and sustain combustion, in example, to get the engine to start.

This vaporization is governed by the fuel's overall volatility, measured by its distillation curve. Within a certain temperature range (that varies with each blend), ethanol decreases the temperature at which the fuel vaporizes, which, theoretically, should help combustion. However, ethanol blends also require more heat to vaporize than gasoline, which means that less vapor than predicted by the distillation curve is actually present inside the cylinder. For example, E10 requires over 15% more heat to vaporize than gasoline. Thus not only the distillation percentage versus temperature, but the heat input required to achieve the temperature are important to understand how fuel differences will interact with the engine design and the operating conditions.

Current fuels are formulated to address this phenomenon. These fuel formulations allow the fuel blend to provide the desired amount of fuel vapor at the temperatures and air pressures typically found in engines to provide the expected starting and hot engine operation characteristics. Other concerns about low temperature fuel characteristics of blends include:

- a) Increased viscosity of ethanol/gasoline blends which may impede fuel flow
- b) Phase separation in the vehicle fuel system due to reduced water solubility

The primary fuel-related concern that occurs at elevated ambient temperatures is vapor lock. Vapor lock is a condition where the fuel in the engine's fuel delivery system vaporizes preventing the required volume of fuel to be delivered. Increasing the ethanol concentration beyond E10 is likely to increase the likelihood of vapor lock for open loop fuel control system engines typically used on older vehicles and most off-road engines. Even in the closed loop engine systems used in some off-road engines and in most late-model vehicles, there remains the likelihood of vapor lock.

### **2.1.3 Change Due to the Enleanment Effect of Ethanol**

Gasoline is a mixture of many hydrocarbon compounds that consist mainly of hydrogen and carbon. Ethanol also contains hydrogen and carbon – but, in addition, it also contains oxygen. The exact air-to-fuel ratio needed for complete combustion of the fuel is called the "stoichiometric air-to-fuel ratio." This ratio is about 14.7 to 1.0 (on weight basis) for gasoline. For ethanol-gasoline blends less air is required for complete combustion because oxygen is contained in the ethanol and because some of the hydrocarbons have been displaced.

For example, for E10 the stoichiometric air-to-fuel ratio is 14.0 to 14.1 pounds of air per pound of fuel. To deliver the required power for any given operating condition engines consume enough air and fuel to generate the energy required, to the limit of the engine's capabilities. Because fuel delivery systems are designed to deliver the prescribed amount of fuel on a volume control basis, the fuel volume delivered is related to the volume of air introduced. The engine design anticipates that the fuel utilized will match the air-to-fuel ratio characteristics utilized in the engine design and calibration. Because ethanol blended fuels require more fuel for the same amount of air to achieve stoichiometric conditions, the fuel system must adapt by introducing more fuel or the desired mixture is not achieved. The effect of this type of fuel change on an engine is called "enleanment." The effect of enleanment depends on engine design and how fuel is metered into the engine.

Since the early 1980s, some automobile engines have used some form of "closed loop" fuel system that continuously monitors and adjusts the amount of fuel delivered to the engine to maintain the stoichiometric air-to-fuel ratio. These vehicles have adjustment ranges that can accommodate oxygenated fuels and, when operating in the "closed loop" mode, may not experience any adverse effects from oxygenated fuels once they have reached operating temperature.

However, during cold start and at full throttle, these vehicles can operate in an "open loop" mode that provides a rich fuel mixture that is necessary for these conditions and to allow the control system to achieve operating temperatures. In the rich mixture, "open loop" mode, vehicles can experience enleanment effects from the oxygenated fuel. While most on-road engines have closed-loop systems, most off-road engines do not. Thus, they have no way to compensate for this enleanment condition.

Lean operation can have several negative attributes including higher combustion temperatures. Even with closed-loop systems, if the fuel contains an amount of ethanol that is outside the system design, the engine similarly may receive too much oxygen and experience performance problems.

#### **2.1.4 Effect on Water Solubility and Phase Separation**

Separation of a single phase gasoline into a "gasoline phase" and a "water phase" can occur when too much water is introduced into the fuel tank. Water contamination is most commonly caused by improper fuel storage practices at the fuel distribution or retail level, or the accidental introduction of water during vehicle refueling. Water has a higher density than gasoline, so if water separates, it will form a layer below the gasoline. Because most engines obtain their fuel from, or near, the bottom of the fuel tank, engines will not run if the fuel pick up is in the water phase layer.

Ethanol-gasoline blends, due to ethanol's greater affinity with water, can absorb significantly more water without phase separation occurring than gasoline. Ethanol blends can actually dry out tanks by absorbing the water and allowing it to be drawn harmlessly into the engine with the gasoline. However, if too much water is introduced into an ethanol blend, the water and most of the ethanol will separate from the gasoline and the remaining ethanol. The amount of water that can be absorbed by ethanol-gasoline blends, without phase separation, varies from 0.3 to 0.5 volume percent. If phase separation were to occur, the ethanol-water mixture would be drawn into the engine and the engine would most likely stop.

## 2.2 Effect on Material Compatibility

A variety of components in engine/equipment systems can come into contact with the fuel. These include:

- Fuel Lines
- Fuel Tanks
- Fuel Pumps
- Fuel Injectors
- Fuel Rails
- Pressure Regulators
- O-Rings
- Gaskets

Materials used in these components should be compatible with the full range of expected fuel composition. Most of metals, rubbers, and plastics that are used in existing engines and fuel system components currently designed to run on E10 fuel blends, where no significant effect to that materials. The compatibility of all of these materials with greater than E10 fuel blends can be predicted from testing on E20 fuels data. Based on the studies, it is clear that several rubbers and elastomers can swell and deteriorate more rapidly in the presence of ethanol. Other materials, such as fluoroelastomers may be able to handle a range of ethanol blends.

Ethanol also corrodes certain metals. Corrosion occurs through different mechanisms including acidic attack, galvanic activity, and chemical interaction. The first is caused by water in the fuel. Ethanol attracts and dissolves water, creating a slightly acidic solution. Unlike gasoline, ethanol alone or combined with water conducts electricity; this conductivity creates a galvanic cell that causes exposed metals to corrode. Another mechanism is direct chemical interaction with ethanol molecules on certain metals.

Effect of fuel line, pressure regulator and fuel pump subjected to E20 [4]

The experiment is focused on conducting materials or component compatibility testing following the SAE standards J1748 (8) (polymeric material) and J1747 (7) (metallic material). The specified testing parameter for the testing is stated under SAE standard. Below are the specifications:

- Test fluids is E20
- Temperature is constant at 55 +/- 2 °C
- 1 Liter-volume test container with burst pressure about 202.7 kPa
- Duration is about 2000 hours



**Figure 1: Fuel line before (left) and after immersion testing with E20**

The fuel line is made from rubber. After experiment, the hose experienced in enlarged diameter, end-delamination and loss of formed shape when immersed whilst shape and size returned upon drying the hoses where typically hardened.

Corrosion happened on a surface of fuel pump (**Figure 2**). The fuel pump surface is made from aluminum. This result proved that current fuel pump is not suitable for ethanol blends fuel with ethanol content greater than E10.



**Figure 2: Corrosion on fuel pump surface resulting from immersion into E20 (left)**



Two general problems associated with using E85 rather than E10 are materials degradation and due to a fact that alcohols are more conductive than gasohol, galvanic corrosion may be happened as the fuel acting as an electrolyte. Materials that degrade in the presence of ethanol blends with high alcohol concentrations include brass, zinc, lead, and aluminum. Corrosion products from material degradation can damage and plug fuel system components. Plastics and rubber components degrade in the presence of ethanol as well. The corrosion behavior [5] of various commonly used materials in the presence of pure ethanol is detailed in **Table 2**.

**Table 2: Corrosion behavior of various metals with respect to ethanol**

Material	Compatibility Issue (Penetration level of)
Aluminum	< 2 Mils/year up to 180°F
Brass	< 20 Mils/year up to 210°F
Bronze	< 20 Mils/year up to 400°F
Carbon Steel	< 20 Mils/year up to 230°F
Copper	< 20 Mils/year up to 110°F
Nickel	< 20 Mils/year up to 200°F
Type 304 S.S.	< 20 Mils/year up to 210°F
Type 316 S.S	< 20 Mils/year up to 420°F
Titanium	< 2 Mils/year up to 200°F

### 2.3 Fuel Delivery System

Fuel is pumped from the tank by an electric fuel pump, which is controlled by the circuit opening relay. Fuel flows through the fuel filter to the fuel rail (fuel delivery pipe) and up to the pressure regulator where it is held under pressure. The pressure regulator maintains fuel pressure in the rail at a specified value above intake manifold pressure. This maintains a constant pressure drop across the fuel injectors regardless of engine load. Fuel in excess of that consumed by engine operation is returned to the tank by way of the fuel return line. A pulsation damper, mounted to the fuel rail, is used on some engines to absorb pressure variations in the fuel rail due to injectors opening and closing.

The fuel injectors, which directly control fuel metering to the intake manifold, are pulsed by the ECU. The ECU completes the injector ground circuit for a calculated amount of time referred to as injection duration or injection pulse width. The ECU determines which air/fuel ratio the engine runs at based upon engine conditions monitored by input sensors and a program stored in its memory.

During cold engine starting, many engines incorporate a cold start injector designed to improve start-ability below a specified coolant temperature. Schematic drawing of the fuel delivery system is shown in **Appendix A-1**.

## CHAPTER 3

### METHODOLOGY

This project has sequence process of works (**Appendix A-1**). The first step is to prepare the fuel blends, E10 and E85. The mixture is base on volume capacity. E10, for example, consists of 10-vol% ethanol and 90-vol% gasoline. Same for E85 which components are 85-vol% ethanol and 15-vol% gasoline. The chemicals involved are industrial ethanol and unleaded gasoline. The next process is to check the material compatibility of some fuel delivery system components by using immersion testing procedure. All of findings will be recorded.



**Figure 3: Ethanol (left) and gasoline**

### **3.1 Preparation of E10 and E85**

Refers to the ASTM 4806 standard, the maximum allowable quantity of water in ethanol solution must not exceed 1% of its total volume. Therefore, water needs to be extracted from ethanol solution. Facility can be utilized is Rotary Evaporator Machine. The Rotary Evaporator Machine is designed to extract one or many fluids from its solution sample, depends on either to collect its sample or product. The machine is applying boiling process where a liquid which lower boiling temperature than water can be extracted.

In this project, the boiling temperature of ethanol is 73.4°C which is lower than water, 100°C. Thus, the machine is applicable for the purpose.

The next step is to prepare the ethanol-gasoline blends, E10 and E85. Ethanol and gasoline is being mixed based on volume composition. Both samples are added into a beaker and were mixed by using a magnetic stirrer.

Separation process might occur in the mixtures. The mixtures are then observed in some period to check on this issue, whilst to ensure that the mixture is homogeneous. The mixing process is done in a close container at room temperature.

### **3.2 Immersion Testing**

The testing and experimental design was not an attempt to fulfill the requirements for material qualification, actual product or process validation for the materials or components. The experiments and testing were in fact designed to highlight any non-compatibility between materials or component and the E10 and E85 blend fuels.

Samples of the component materials consists of fuel line, pressure regulator and fuel injector, are weighted before undergo the experiment. This record is check whether mass reduction happen or not.

This testing is also required close-containers, material samples and E10 and E85 as test fluids. The material samples will be immersed into the E10 and E85 fuels in a separate container respectively. From an established experiment, higher temperature can be helped as an accelerant [7]. However, applying this testing at high temperature required extensive monitoring cautions due to behavior of the fuels; high flammable.

In this project, the experiment has been done in room temperature circumstances. The duration of the testing is about 4 weeks. Thus, the condition of the material samples as well as the testing fluids is monitored and compared between the beginning data and the findings.

### **3.3 Microscopic Examination**

The microscopic examination need to be done only before and after the immersion testing. The rust of the sample is firstly needed to be removed from the sample surface. This is to ensure that the surface is flat and easy for microscopic examination. During microscopic examination, optical microscope will be utilized. Surface structure of the sample before and after the immersion testing is then being compared. The surface of the sample will be zoom-ed in up to **50X** scale.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Removing water from ethanol solution:

Boiling temperature of water is  $100^{\circ}\text{C}$  while ethanol is  $73.4^{\circ}\text{C}$ . In the end of the experiment, entire ethanol was evaporated. The ethanol is proved that contain 0-vol%, or less, of water and suitable to be blend with gasoline. (**Appendix A-2**)



**Figure 4: 100-vol% ethanol (after vaporization process)**

## 4.2 Observation on separation process

After the mixing process, both beakers containing E10 and E85, respectively, are observed for any occurrence of separation process. For 4 weeks of observation, no separation occurred in both containers.

## 4.3 Immersion Testing

**Table 3: Mass of samples before and after the experiment**

Sample	Mass (gram)			
	Week 0		Week 4	
	E10	E85	E10	E85
Aluminum (Fuel regulator)	7.919	8.046	7.918	8.039
Steel (Injector Nozzle)	2.465	2.464	2.465	2.463
Rubber (Oil Ring)	0.174	0.173	0.174	0.167

Percentage of mass reduction:

Aluminum:

$$\text{E10; } (7.919 - 7.918) / 7.919 * 100\% = \mathbf{0.013 \%}$$

$$\text{E85; } (8.046 - 8.039) / 8.046 * 100\% = \mathbf{0.087 \%}$$

Steel:

$$\text{E10; } (2.465 - 2.465) / 2.465 * 100\% = \mathbf{0.000 \%}$$

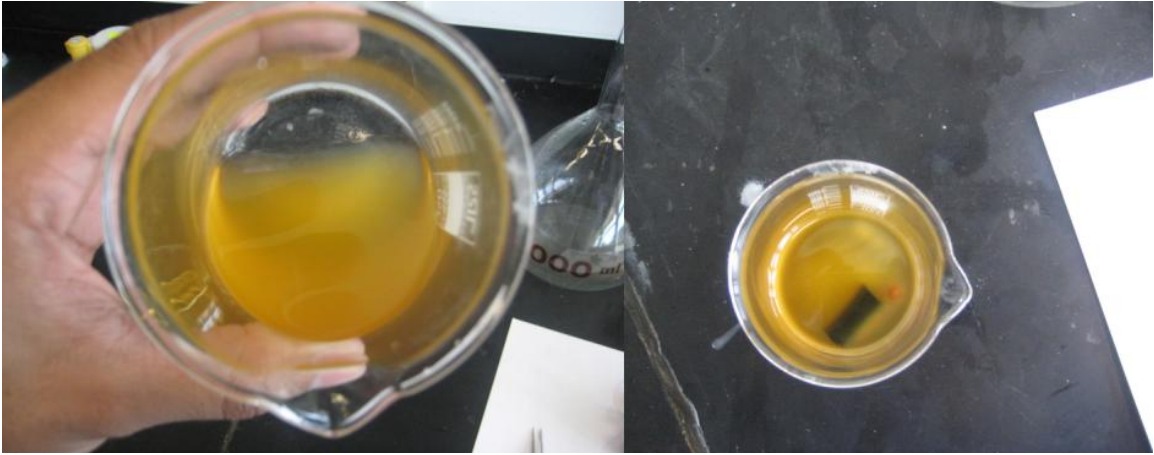
$$\text{E85; } (2.464 - 2.463) / 2.464 * 100\% = \mathbf{0.041 \%}$$

Rubber:

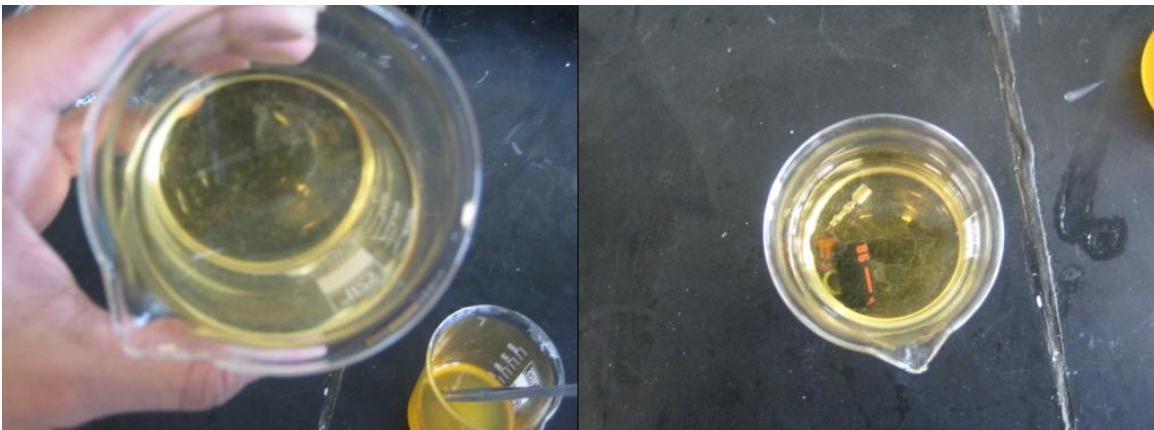
$$\text{E10; } (0.174 - 0.174) / 0.174 * 100\% = \mathbf{0.000 \%}$$

$$\text{E85; } (0.173 - 0.167) / 0.173 * 100\% = \mathbf{3.468 \%}$$

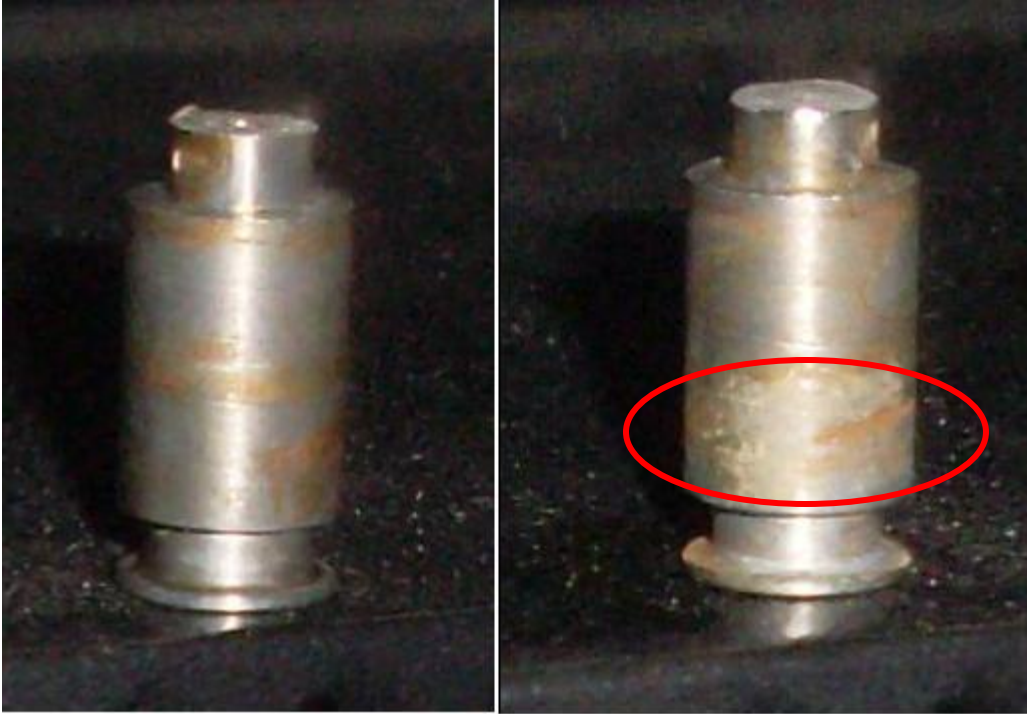




**Figure 5: A beaker containing material samples with E10 as testing fluid**



**Figure 6: A beaker containing material samples with E85 as testing fluid**



**Figure 7: Effect on the existing corrosion on the fuel injector sample. Left (E10), right (E85)**



**Figure 8: Corrosion at fuel regulator (E85)**

The testing data shows that the E10 and E85 test fuels demonstrates potential incompatibility with selected fuel system components. These findings are based on visual inspection and physical measurement on the samples after 4 weeks of immersion period.

There are several changes occurred within the physical properties of the fuels and also the material samples. The changes that can be observed are:

1. Mass reduction
2. Colour of the fuels
3. Corrosion at metal surfaces

Generally, if the fuel system components immersed in the gasoline test fuel showed some change in appearance, so would the same component in E10 and E85. This is not considered to be of significant concern. It is only when the component immersed in E10 and E85 is the only one to show a change in appearance which incompatibility needing be suspected.

The very noticeable result is on the mass reduction. Referring to established studies, E10 has gives no affect to material of conventional vehicle. Thus, there should not have mass reduction within the process and the result from this experiment might due to some error in mass equipment. Meanwhile, ethanol-gasoline blends with ethanol vol% greater than E10 is said to have side effect to vehicle fuel delivery system component especially metals. The effect is degradation in the form of corrosion, surface cracking, fatigue etc.

Corrosion of metallic fuel system component is considered a concern since the potential exists for the oxide to dislodge and become trapped in between moving components. This situation would most likely result in accelerated wear of these components surfaces. This is also considered a concern if the potential exists for the oxide to dislodge and block other fuel system components thus impairing their functioning to specification. The potential exists, depending upon the severity of the oxidation and the actual final location of the dislodged oxide, to cause engine failure.

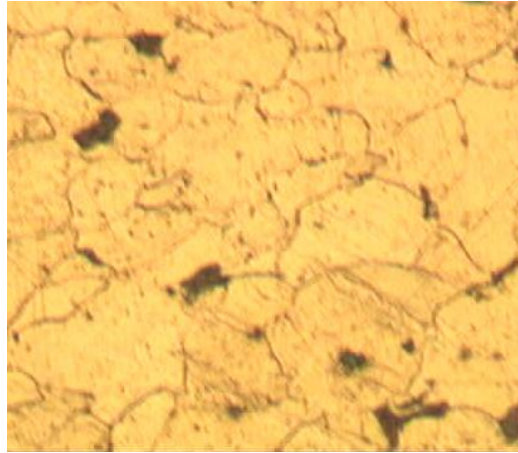
Second observation is on the colour of the fuels. E10 and E85 are initially in clear dark-yellow and light-yellow respectively. The colour, however, has been changed from clear yellow in E10-containing beaker to blur yellow. The possibility of the changed is said to be erosion of existing rust on the surface of the components. In fact, E10 has no effect with metal degradation as the concentration of the ethanol is lower. Therefore, it can be conclude that there might be corrosion occurred during the experiment as the final result has not been further analyze in term of current and electron transferred, if any, and chemical properties.

In the E85 beaker, there are much suspended particles within the solution. The suspended particles are suspected comes from elements of the metal samples that had been wear-out. This result might prove that the oxidation process was there within the solutions. Oxidation process is a process involving mass and electron transferred. This process is also known as mass reduction process where lower electro-negativity component discharged its electron as well as its particles into a conductive fluid. In term of material defect, this process is resulting in material degradation in term of corrosion.

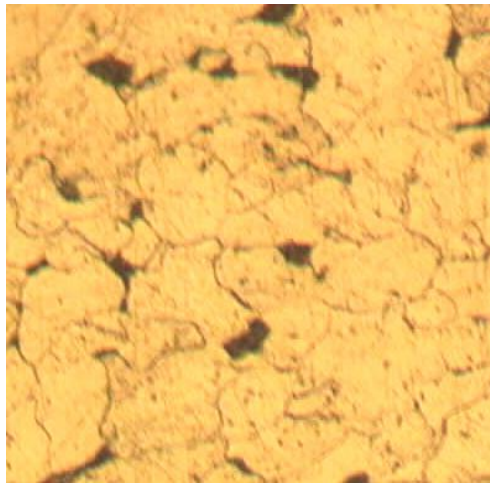
Rubber material (O-ring gasket for fuel injector) is found to have significant changes in appearance due to contact with the fuels. After the experiment, the rubber has lost its elasticity and become hardened. This is considered as unacceptable since the changes have the potential to result in fuel leakage

The last observation of the experiment is about the corrosion rate. **Figure 7** tells us that metal subjected to E85 experienced will be corroded. White rust can be seen from this experiment; informing that the rust area has been oxidized. The oxidation process is easy to occur at the rusty surface of the material sample. It is because electrons can be transferred at the lowest load-density surface or non-treatment surface. The electrons are bonded weakly, thus it will be easy to be transferred.

#### 4.4 Microscopic Examination



**Figure 9: Surface structure of injector metal before the immersion testing (50X)**



**Figure 10: Surface structure of injector metal after the immersion testing (50X)**

By comparing before and after immersion testing, the surface structure of the injector metal did not show any significant changes. However, this result can be further examined to know any effects within its microstructure.

## **CHAPTER 5**

### **CONCLUSION**

As a conclusion, E10 has been currently proved that has no effect with material of fuel system component. This fuel can be further investigation as the complete characteristic of the fuel is not yet available in particular in term of chemical perspective.

Differ to E85, with the high percentage of ethanol within the mixture, it is said to have some affects to the fuel system components. The affects are material degradation which it may lead to metal corrosion and wear. These affects is due to the electrochemical process occurred within the control system pertaining the fuel, conductive metal of the system and also close system (no external effect). This study has thus achieved its objectives.

## **CHAPTER 6**

### **RECOMMENDATION**

On the other hand, more extensive study can be performed to evaluate the properties of the fuel especially ethanol blends with ethanol percentage higher than 10vol%. The study can be made in chemical and electrical fields. This is because the corrosion rate can be calculated based on the rate of electron transferred, properties of the conductive element, density of voltage and current flows (Tafel Calculation).

In term of microstructure, Scanning Electro Microscopes (SEM) can be utilized to evaluate the microstructure of a sample prior to recommends other alternatives material to replace the material of conventional fuel delivery system components.



## **CHAPTER 7**

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## APPENDIX

### APPENDIX A-1: Schematic Drawing of Fuel Delivery System

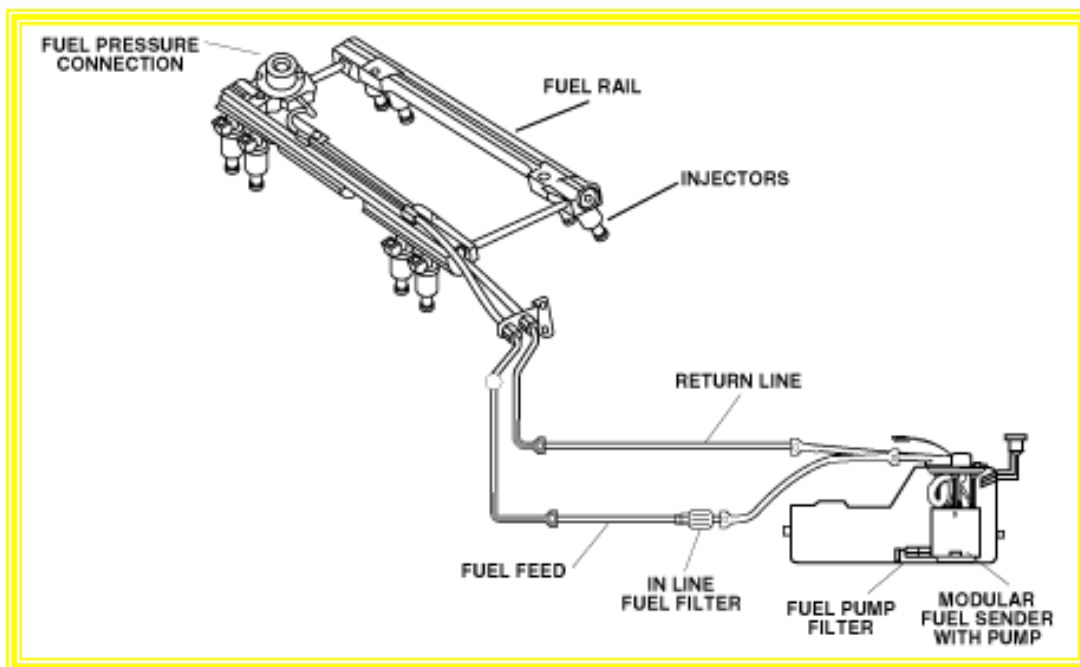
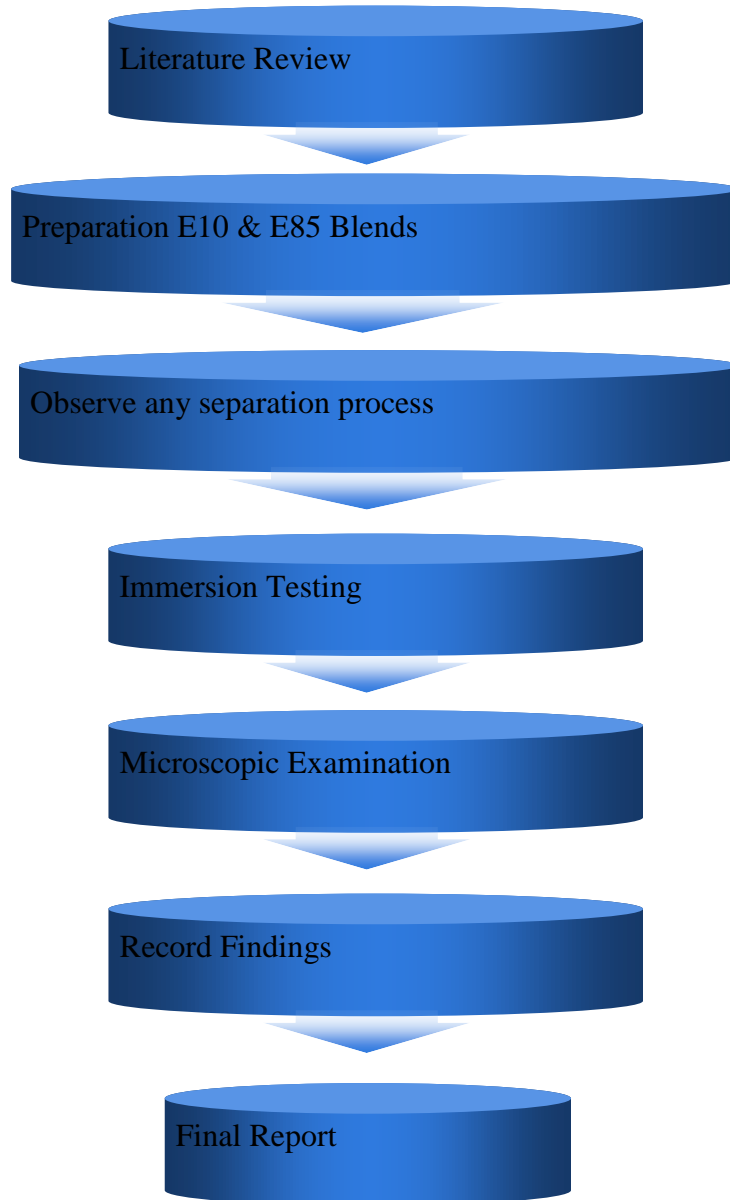
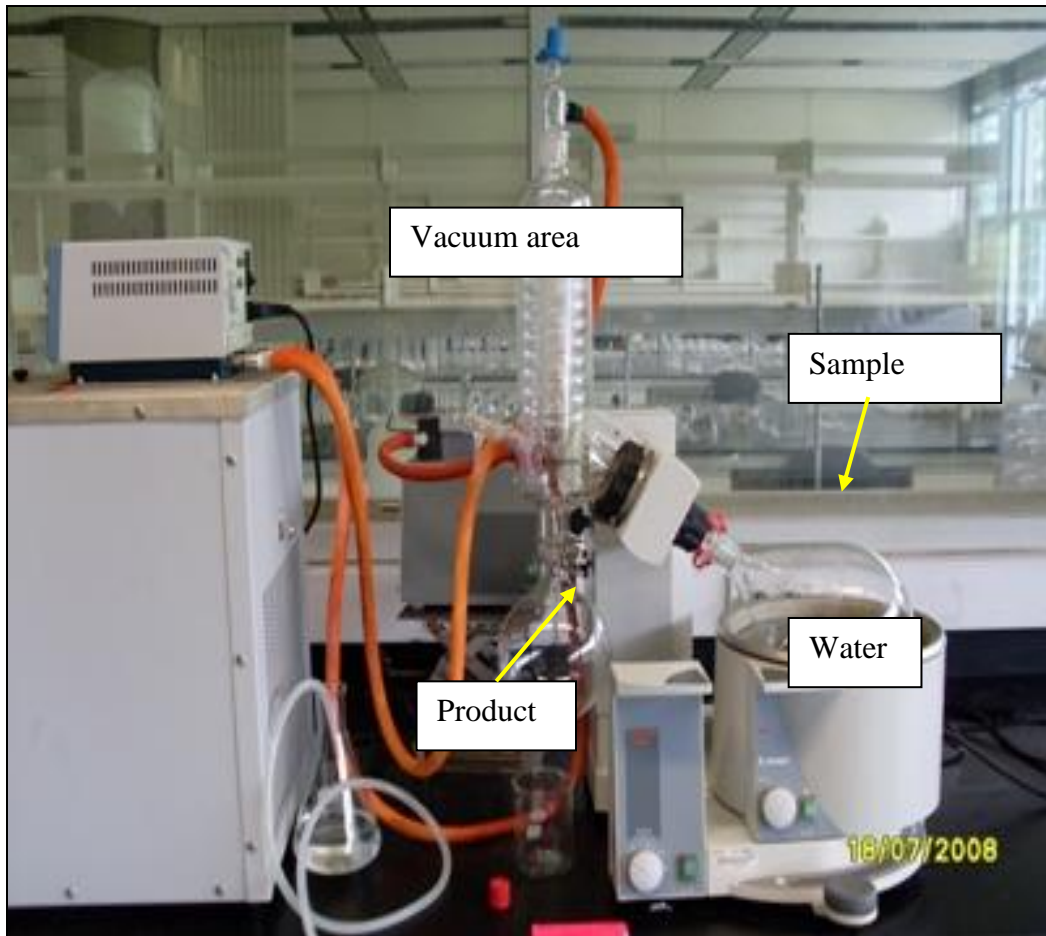


Figure 11: Schematic drawing of the critical fuel delivery system of a car

## APPENDIX A-2: Flow of project works



### APPENDIX A-3: Rotary Evaporative equipment



**Figure 12: Rotary Evaporator Equipment**