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THE EFFECT OF ETHANOL ON FUEL TANK CORROSION RATE

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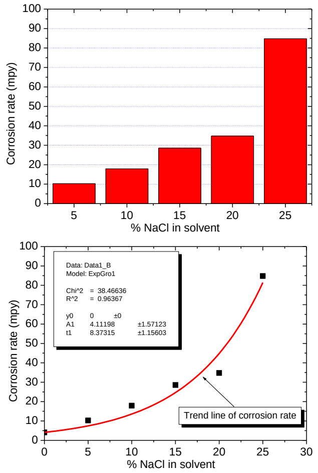
Graphical abstract



Abstract

In recent decades, the use of ethanol as an alternative fuel for S.I engines has become a popular issue. This is not only due to availability and oil prices, but also to address concerns about the increase in greenhouse gas effects. However, ethanol is corrosive in a fuel tank made of metal, because it contains soluble chloride ions. Therefore, this paper presents the results of an investigation of the fuel tank corrosion rate made of metal FE_U_100 due to the use of pure ethanol. The test was performed by PGS-120T potentiostat with the addition of NaCl in ethanol in concentrations of 5, 10, 15, 20, and 25% while the estimated corrosion rate on pure ethanol was done by regression. The estimation of the fuel tank corrosion rate through the exponential regression for the use of pure ethanol is 4,116 mpy. Then, from the assessment metrics, the fuel tank made of Fe_U_100 has corrosion resistance in the excellent category. This means no fuel tank modification or replacement is required for pure ethanol applications in S.I. engine.

Keywords: Ethanol, S.I. engine, fuel tank, potentiostat, corrosion rate

1.0 INTRODUCTION

In the last few decades, the availability of fossil fuels has been a concern of many stakeholders [1-2]. Crude oil products from current production fields may have passed the peak of production. The peak oil issues will cause oil to become scarce, the cost and demand of oil products will increase, while the supply is limited [3-5]. In addition to oil production, another crisis issue is related to global climate change caused by the burning of fossil fuels. If it is not controlled, the costs and challenges of reducing greenhouse gas (GHG) emissions will increase along with time. To overcome the climate changes and greenhouse gas emissions, one effective way is to act immediately in ~~to~~ replacing fossil fuels with renewable fuels, such as ethanol/bioethanol for Spark Ignition (S.I.) engines and Compression Ignition (C.I.) engines [6-7]. The application of ethanol in the S.I. engine is relatively easier and can be accepted by all types of Ligh Duty Vehicles (LDVs). However, the applications on C.I. engines must be accompanied with some engine modifications and the use of cetane enhancers[8]. Nevertheless, some researchers report that the addition of 10% ethanol in diesel engines is capable of producing better engine performance and emissions [9-11].

In the early years of the history of car (about a century ago), ethanol did not promise to be used because its production was insufficient and its price was uneconomical. However, with the advanced production technology and can be made widely from biomass, one day the price can compete with high-quality fossil fuels [12]. As explained earlier, the use of ethanol begins from an awareness of the depletion of petroleum reserves. On the other hand, the use of ethanol is to improve the air quality, especially in urban areas [13]. The comparison of ethanol to gasoline and methanol properties is given in Table 1.

In the last decade, ethanol production for road vehicle sector is increasing [14-15], which means it brings a positive impact on local and regional economies [9]. However, large-scale production will be constrained by the availability of land for food production. Ethanol is commonly used as a blend in gasoline with the concentrations of 5% to 85% (E5, E85) [8], although it can be identified as a full dedicated fuel (100%). The use of Ethanol has become an energy policy in several countries such as Brazil, the United States, Argentina, and some countries in the Americas and Europe [3]. Now, many countries are pushing to sell gasoline-alcohol mixtures in fuel stations because fuel oil causes high exhaust emissions, including gases like CO (carbon monoxide), CO_2 (carbon dioxide), NOx (nitrogen oxides), and particulates.

Table 1 Comparison of ethanol to gasoline and methanol [16]

Fuel	**Gasoline**	**Ethanol**	**Methanol**
Typical formula	$C_{6.97}H_{14.02}$	C_2H_5OH	CH_3OH
Density (kg m^{-3} at 15°C)	750.8	809.9	796
Research octane number	95	108.6	108.7
Motor octane number	85	89.7	88.6
Kinematic viscosity (mm^2 s^{-1} at 40 °C)	0.494	1.221	0.596
Heating value (kJ kg^{-1})	42.6	26.7	19.85
Heating value (MJ m^{-3})	31.985	21.625	15.8
Distillation%			
Initial boiling point	45	78	64
50	96	78	64
90	168	79	65
End boiling point	207	79	66

Initially, vehicles that run by gasoline-ethanol blend produce less power than the use of pure gasoline. In line with research and development activities to improve compression ratio, injection time, and ignition time, the problem in power loss can be reduced[16-17]. Ozsezen and Canakci [18] tested an alcohol-gasoline mixture on S.I. The result shown that the engine power was slightly increased compared to pure gasoline. Indeed, the fuel consumption of the alcohol-gasoline mixture is slightly higher than that of pure gasoline to achieve the same power. However, the gasoline-alcohol mixture at all vehicle speeds gives slightly higher combustion efficiency compared to pure gasoline.

Moreover, ethanol is not as strong as gasoline, which means there are problems during winter or in extremely cold weather. However, there are solutions ~~to~~ for this problem, including adding additives or adjusting the percentage of concentration at cold start condition [11]. As an alternative fuel, ethanol has the advantage of being renewable and has an octane rating higher than gasoline. It is possible to apply ethanol ~~to~~ in a high compression ratio (up to 19.5) to improve thermal efficiency and exhaust emissions. In fact, for high-concentration ethanol applications, the modifications required not only in compression ratio, but also in some engine components in order for the vehicle to run smoothly and prevent them from damage. In a study that used a complex engine control system and an optimized exhaust recirculation system, a car running on the E50 is capable of producing fuel efficiency equivalent to a gasoline car [19]. Table 2 presents the engine and vehicle components that must be adjusted in the application of ethanol blend from low to high concentration.

Table 2 Resetting on a S.I. engine to use ethanol fuel [20]

<table>
<tr><th>Etanol consentration</th><th>Carbu-retor</th><th>Injec-tor</th><th>Fuel pump</th><th>Pressure regulator</th><th>Fuel filter</th><th>Ignition system</th><th>Evaporation system</th><th>Fuel tank</th><th>Catalitic Conv.</th><th>Engine oil</th><th>Intake system</th><th>Exhaust System</th><th>Cold start system</th></tr>
<tr><td>≤ 5%</td><td colspan="13">🟦 All Vehicles</td></tr>
<tr><td>E5-E10</td><td>🟧</td><td colspan="12">🟦 All vehicles are less than 20 years</td></tr>
<tr><td>E10-E25</td><td colspan="9">🟧 Vehicles specially designed for ethanol applications</td><td colspan="4">🟦</td></tr>
<tr><td>E25-E85</td><td colspan="12">🟧 Vehicles specially designed for ethanol applications</td><td>🟦</td></tr>
<tr><td>E85-E100</td><td colspan="13">🟧 Vehicles specially designed for ethanol applications</td></tr>
<tr><td colspan="3"></td><td colspan="3">🟦 No modifications required</td><td colspan="3"></td><td colspan="2">🟧 Modifications may be required</td><td colspan="3"></td></tr>
</table>

However, Ethanol contains soluble and insoluble elements [21]. The soluble element is chloride ions which have corrosive properties. Ions will attack the passivation of the oxide film on the metal so it will corrode and increase the fuel conductivity. Soluble elements, such as aluminum hydroxide, will clog the fuel system. Ethanol is hygroscopic which absorbs moisture directly from the atmosphere. The water content in ethanol will decrease the combustion energy and cause knocking on the engine. To avoid such risks, the ethanol must be sealed during storage. However, this procedure becomes difficult because the fuel tank should be provided ventilation valve to prevent vacuum.

Corrosion will damage metals, including fuel tanks, fuel system components made of plastic and rubber, injectors, and emerging deposits. In 2001, several models of vehicles that used alcohol fuels in Japan reportedly experienced fuel leaks and fires due to corrosion in fuel system components made of aluminum. Then, an investigation is done by a team. To prove the case, the immersion test was performed on metals and other materials used for the fuel system part to determine the corrosion resistance of ethanol contained in the fuel. The results of this study indicate that a high concentration of ethanol cause corrosion in the fuel system components made of aluminum [22]. Other studies related to the effects of ethanol on the corrosion of fuel tanks and fuel pipelines also have been done by Singh, Rawat, Kane, and Matějovský [23-26].

In 2015, a team from the Gasoline and Diesel Engines Laboratory of Universitas Muhamadiyah Magelang has tested the fuel tank corrosion rate due to the E10 to E30 applications. The method used is by conventional immersion method to the sample of the fuel tank for two months. Each week the sample is removed, cleaned, and checked for weight loss. However, this method has not provided valid corrosion rate data due to the limitation on equipment [27]. Therefore, as a follow-up of the previous study, this research is to test the corrosion resistance of fuel tank using the potentiostat method.

2.0 METHODOLOGY

2.1 Specimen Preparation

In this study, a tank was cuted into test specimens. Some of the specimens were subjected to a material composition test using IK 5.4-1-1 method in the Metal Testing Laboratory at the Ceper Manufacturing Polytechnic, Klaten, Indonesia. The result of material composition shows that the fuel tank tested is a steel with Grade Fe_U_100. Then, the other pieces are formed in a circular dish with an area of 170 mm^2 as shown in Figure 1. The specimen's surface is then smoothed and polished with 1000 mesh sandpaper.

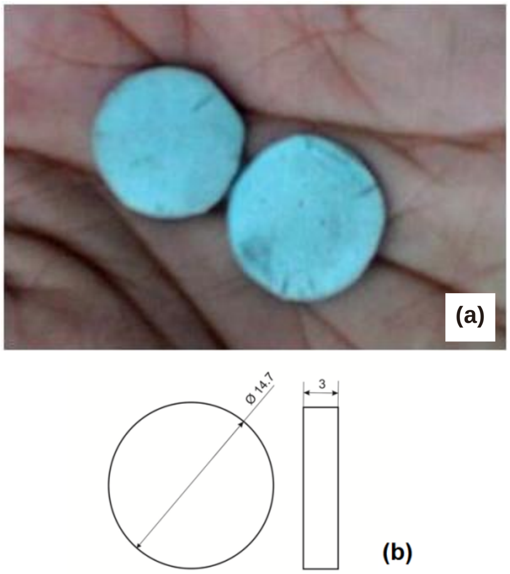


Figure 1 The specimens of fuel tank: (a) Photographic view of the specimens and (b) the dimension of specimen (in mm)

2.2 Corrosion Solvent

After the specimens are completed, the next step is ~~to~~ preparing the solvent to test the corrosion resistance. Since ethanol can not conduct an electric current, NaCl is added to the ethanol. Variations in the ethanol-NaCl used are shown in Table 3.

Table 3 Solvent for corrosion testing

Sample	Solvent	% NaCl in solvent
090/P/STA/17	Ethanol 190 ml +10 ml NaCl	5
	Ethanol 180 ml +20 ml NaCl	10
	Ethanol 170 ml +30 ml NaCl	15
	Ethanol 160 ml +40 ml NaCl	20
	Ethanol 150 ml +50 ml NaCl	25

2.3 Test Equipment

The corrosion test apparatus used is the PGS-201T potentiostat as shown in Figure 2. The testwas conducted at the National Nuclear Power Agency, Yogyakarta, Indonesia. The specimen is attached to the working electrode with a shiny surface facing out to be immersed in the solution Then, it was attached to the electrochemical cell. The columnel and platinum electrodes are mounted on the electrochemical cell. A 200 ml corrosion solution is introduced into the electrochemical cell until all electrodes are dyed. Then, all electrodes are connected to the IMT-1 interface. IMT-1 program is an interface code of the computer as a device of the PGS-201T potentiostat). Potentiostat and IMT-1 interface is turned on until the process of data transfer on the microcomputer.

Measurements were made by giving a working electrode potential of -2000 mV to +2000 mV with a scan rate of 20 mV/s through the operation of a microcomputer that provides the output of a potential curve versus the log of current intensity. All solutions, before and after treatment measured its conductivity and PH. All measuring activities are carried out at room temperature of 25 ^{0}C.

Figure 2 Potensiostat equipment

2.4 Corrosion Rate Calculation

By using the electrochemical method, the corrosion rate is measured based on the potential difference of the object to obtain the corrosion rateoccured. This electrochemical method uses the formula based on Faraday's Law presented in equation (1)[28].

$$CR = K\frac{aI}{nD} \tag{1}$$

Where, CR is corrosion rate (mpy), K is constant factor (mpy=0.129), a is atomic weight of metal, I is current density (μA/cm^2), n is number of electron loss, and D is metal density (g/cm^3).

3.0 RESULTS AND DISCUSSION

3.1 Test Result

In this study, the corrosion testing was performed alternately for 5 samples with one test instrument. The results of corrosion testing are presented in Figure 3, which indicates that higher levels of NaCl in ethanol increased the current density. After corrosion test data was known, then, the calculation of corrosion rate was done by considering material density and atomic valence obtained from composition test. The corrosion rate is presented in Table 4 and Figure 4, respectively. It is seen that the increase of NaCl content in the solution followed by an increase in corrosion rate.

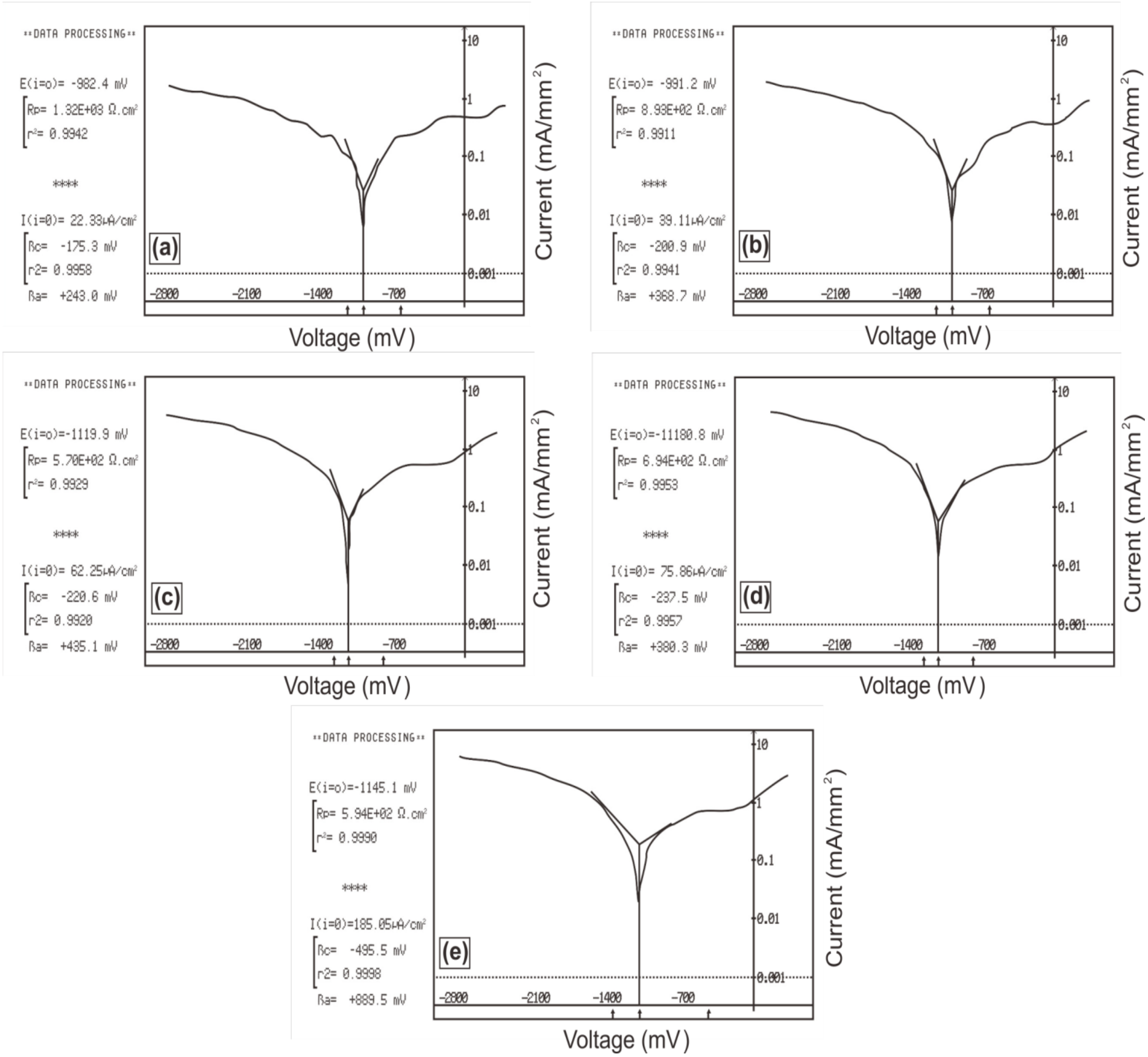


Figure 3 Corrosion test results for all solvents used: (a) 5 % NaCl (I=22.33 μA/cm2); (b) 10 % NaCl (I=39.11 μA/cm2); (c) 15 % NaCl (I=62.25 μA/cm2); (d) 20 % NaCl (I=75.86 μA/cm2); and (e) 20 % NaCl (I=75.86 μA/cm2)

Table 4 Corrosion rate calculation

Solvent	% NaCl in solvent	Atomic weight	Current density	Atomic valence (Fe_U_100)	Metal density	*K*	*Corrosion rate, CR* (mpy)
		a=M	*I*	*n*	*D*		
Ethanol190 ml+10 ml NaCl	5	55,845	22,33	2	7,86	0.129	10,23316995
Ethanol180 ml+20 ml NaCl	10	55,845	39,11	2	7,86	0.129	17,92294119
Ethanol170 ml+30ml NaCl	15	55,845	62,25	2	7,86	0.129	28,52730988
Ethanol160 ml+40 ml NaCl	20	55,845	75,86	2	7,86	0.129	34,76436510
Ethanol150 ml+50 ml NaCl	25	55,845	185,95	2	7,86	0.129	84,80287056

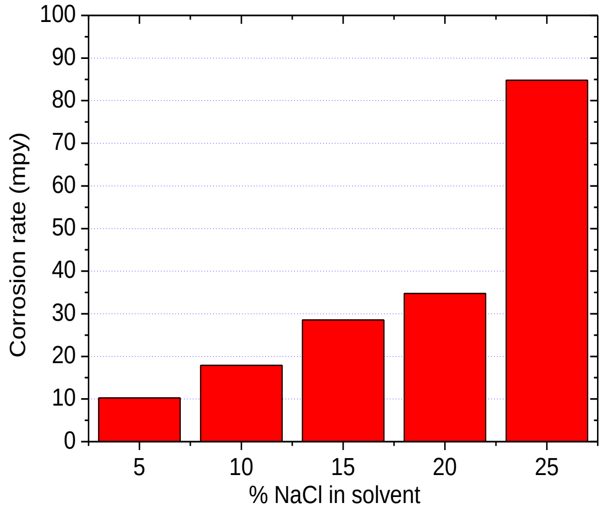


Figure 4 Percentage of NaCl in solvent to the trend of corossion rate

3.2 Corrosion Rate Estimation for Pure Ethanol

To determine the corrosion rate in pure ethanol by using an exponential regression with response (y) and predictor (x) obtained from Table 4. Where, the value of x is the percentage of NaCl in the solvent and y is the corrosion rate in mpy. The exponential regression obtained from software Origin 6.0 is $y = y_0 + A_1 e^{\left(\frac{x}{t1}\right)}$, where the value A_1 is 4.166 and *t1* is 8.37. Thus, the corrosion rate for pure ethanol can be estimated as follows.

$$y = y_0 + A_1 e^{\left(\frac{x}{t1}\right)}$$

$$y = 0 + (4.166)e^{\left(\frac{0}{8.37}\right)}$$

$$y = 4.166\ [mpy]$$

In graphical form, the exponential curve of the corrosion rate is presented in Figure 5.

In another recent study conducted by Thangavelu *et al.* [29], ethanol effects on corrosion rates on materials made of mild steel (0.2% C, 0.4% Mn and 99.4% Fe), copper (99.99%) and aluminum (99% commercially pure) were studied. A submersion method was performed to test the material's resistance to exposure to ethanol mixed in low-grade biodiesel. The results of this study show that the corrosion rates for E5 and E10 at room temperature are 0.1572 and 0.1817 mpy, respectively. If this result is extrapolated linearly to E100, the corrosion rate at E100 is about 0.6627 mpy. This study also concluded that mild steel(MS) corrosion resistance is better than Aluminium (Al) but worse than copper (Cu).

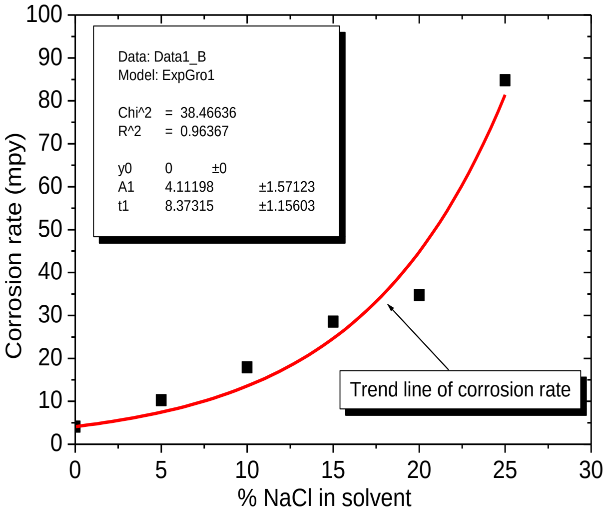


Figure 5 Exponential regression of corossion rate

In the present study, a corrosion rate of 4,166 mpy showed a lower value than the results of investigations conducted by Rawat [22] who reported a corrosion rate on carbon steel exposed 100% ethanol (E100) was between 10 and 12 mpy. Meanwhile, with the addition of an inhibitor, the corrosion rate can be reduced to 4-5 mpy.

3.3 Corrosion Resistance Analysis

After the corrosion rate is known, then, an assessment of the corrosion resistance of the tank is performed. The assessment is divided into 6 categories: outstanding, excellent, good, fair, poor, and unacceptable, respectively. The parameters used to assess are presented in Table 5.

Table 5 Corrosion resistance assessment matrix [28]

Relative Corrosion Resistance	***Aproximate Metric Equivalent***				
	mpy	**mm/year**	**µm/year**	**nm/year**	**pm/sc**
Outsatnding	< 1	<0.02	<25	<2	< 1
Excellent	1-5	0.02-0.1	25-100	2-10	1-5
Good	5-20	0.1-0.5	100-500	10-50	5-20
Fair	20-50	0.5-1	500-1000	50-100	20-50
Poor	50-200	1-5	1000-5000	100-500	50-200
Unacceptable	200+	5+	5000+	500+	200+

The estimation of the fuel tank corrosion rate through the exponential regression for the use of pure ethanol is 4.116 mpy. Then, from the assessment metrics, the fuel tank made of Fe_U_100 has corrosion resistance in the excellent category. This means no fuel tank modification or replacement is required for the pure ethanol applications in S.I. engine.

4.0 CONCLUSION

The results of this study indicate that the fuel tank made of Fe_U_100 has excellent ability against corrosion attack due to the use of pure ethanol. The estimated corrosion rate obtained by exponential regression for the use of pure ethanol is 4,116 mpy. In the relative corrosion resistance metrics, the corrosion rate of 4,116 is categorized as "excellent". This research will continue with the inspection of other fuel components such as pipe line, injector, pressure regulator diaphragm, and fuel pump.

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