

Estimation method of heating value properties on variations of alcohol-gasoline blends and volume percentages

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ABSTRACT

Heating value has been one of the important properties of gasoline surrogate fuel being investigated for thermal conversion system inside combustion cylinder. Alternative fuel yielded from biomass is expected to have lower energy content than baseline fuel (gasoline), as several factors were analysed such as molecular structure and carbon contents. Qualifying fuel's heating value properties can serve the researchers who work on different alternative fuels to indicate the fuel suitability for spark-ignition engines according to fuel standards. This research work was conducted to study the effects of alcohol blends (methanol, ethanol and iso-butanol) at different volume percentages (0-25%) with an interval of 2.5% on the heating value of gasoline fuel. A non-linear relationship was observed for heating value of each fuel blend generated from statistical polynomial regressions with the highest order of two. Polynomial equations derived were expected to be highly accurate in estimating the properties of heating value of the fuel blends as the coefficient of determination obtained for methanol, ethanol and

iso-butanol blends were 0.9445, 0.9691 and 0.692, respectively. Analysis based on the percentage error was done using average absolute error and average bias error with those blends producing lower than 2% error. The estimation model is suggested to be used as it produces highly accurate and precise results for the alcohol-gasoline blends.

Keywords: *estimation method; alcohol-gasoline blends; physicochemical properties; heating value, combustion characteristics.*

Introduction

Physicochemical properties such as kinematic viscosity, density and heating value are important properties that need to be utilized in optimizing the combustion behaviour, engine performance and exhaust emissions of either spark-ignition or compression ignition engine. Analysis for estimating the properties of parameters related to its chemical structure has been made since 1960s by Gouw and Vlugter [1]. They investigated the relations of density and molar volume of fatty acid methyl ester (FAME) at 20°C using Smittenberg relation. This relation was used to express the physical constants to a homologous series of hydrocarbons [2]. Prediction of viscosity for fatty acid methyl ester composition has been proposed by C. A. W. Allen et al. [3] with verifications using controlled mixtures of natural biodiesels and standard fatty acid esters. The Grunberg-Nissan model [4] has been used by the authors to develop binary mixtures and optimally works for non-associated liquids.

Heating value has been classified into two bases; higher heating value (HHV) and lower heating value (LHV). HHV determines the gross calorific value in which the heat released from the fuel is in the state of liquid. Meanwhile, LHV regulates the net calorific value based on the heat generated from the gaseous liquid as the product [5]. In accordance to ASTM D240-09 [6] for the standard test method for heating value of hydrocarbon fuels by bomb calorimeter, HHV and LHV are related to each other as shown in Equation (1):

$$Q_{net}(LHV, 25^{\circ}C) = 10.025 + (0.7195)Q_{gross}(HHV, 25^{\circ}C) \quad (1)$$

Where Q_{net} = Net heat released during combustion process, MJ/kg
 Q_{gross} = Gross heat released during combustion process, MJ/kg

Alternative fuels have lower energy content compared to gasoline resulting from its chemical structure. The utilization of these fuels that have less energy content usually causes a reduction in the engine output power

with higher specific fuel consumption. Therefore, the energy content is currently one of the major technical issues in the use of different alternative fuels as it relates to the engine power. However, the conducted researches on measuring the energy content were very limited and did not indicate the methods and equipment used for measurement. Moreover, the information concerning the energy content determination of different fuels remains scarce.

C. Sheng and J. L. T Azevedo [5] analysed higher heating value of biomass fuels based on three types of analyses; ultimate, proximate and chemical composition. Statistical evaluations from a larger database were collected from open literature as it was found that the correlations based on ultimate analysis are the most accurate with average absolute error (AAE) of less than 7% compared to those of proximate and chemical composition analyses. Comparisons between those analyses of estimating higher heating values have been investigated throughout the previous studies [7-10]. In general, the estimation methods have been divided into three groups with certain elements of carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O):

- 1) Consideration of 5 elements (C, H, N, S, O) [11].

$$\mathbf{HHV} = 35.2\mathbf{C} + 116.2\mathbf{H} + 6.3\mathbf{N} + 10.5\mathbf{S} - 11.1\mathbf{O} \quad (2)$$

- 2) Consideration of 3 elements (C, H, O) [12].

$$\mathbf{HHV} = 30.1\mathbf{C} + 52.5\mathbf{H} + 6.4\mathbf{O} - 76.3 \quad (3)$$

- 3) Consideration of 1 element (C) [13].

$$\mathbf{HHV} = 43.7\mathbf{C} + 167.0 \quad (4)$$

Heating value has brought several key roles in determining the quality of the fuel on gasoline engine performance, combustion behaviour and exhaust emissions [14, 15]. Such implications of heating value have been listed in Table 1.

In part of the energy production for alcohol-gasoline blend, ethanol-gasoline blends have slightly the same effects as the methanol-gasoline blends. M. Koc et al. [16] evaluated the engine performance and emission characteristics of a single cylinder four-stroke spark-ignition engine fuelled with ethanol-gasoline blends (50% and 85% of ethanol). The authors concluded that ethanol-gasoline blends produced higher brake specific fuel

consumption (BSFC) than pure gasoline relying on the volume percentage of ethanol. This was attributed to the lower brake power produced by the fuel blend in which that LHV of the fuel is the main factor contributing to these findings [17-20]. These findings can be supported by the research conducted by Simeon Iliev [21] who has developed a 1-D combustion model using AVL BOOST for simulating a four-stroke, port fuel injection, spark-ignition engine fuelled with methanol and ethanol-gasoline blends. The combustion model was used to estimate the influence of the fuel blends with a variety of volume percentage on engine performance and exhaust emissions. In comparison to pure gasoline fuel, ethanol-gasoline blends produced lower engine brake power as the heating value of ethanol is lower than that of gasoline fuel.

I. M. Yusri et al. [22] compared the effects of 2-butanol-gasoline blends at half throttle position at 3 different volume percentages (5%, 10% and 15%) on combustion characteristics of cylinder pressure, rate of heat release (ROHR) and average indicated mean effective pressure (IMEP). The results showed that the fuel blends have reduced the cylinder pressure at all volume percentages. Comparing between gasoline-butanol blends, GBU5 (gasoline 95% - butanol 5%) has the lowest pressure with 19.8 bar, followed by GBU10 (gasoline 90% - butanol 10%) and GBU15 (gasoline 85% - butanol 15%) at 20.3 and 20.8 bar, respectively. These results contributed to the increasing volume percentage of 2-butanol in the fuel blends which were also related to the ROHR and average IMEP produced [23].

I. Gravalos et al. [24] examined the emission characteristics of a single cylinder spark ignition engine fuelled with lower-higher molecular mass alcohol-gasoline blends. The blends consisted of C₁-C₅ alcohol with approximately 1.9% methanol, 3.5% propanol, 1.5% butanol, 1.1% pentanol and variable volume percentage of ethanol with pure gasoline fuel at the engine speed of 800-1600 rpm. The results showed that lower-higher molecular mass of alcohol-gasoline blends emitted lower CO and HC emissions compared to those of pure gasoline fuel. In contrast with the behaviour of CO and HC emissions, exhaust emissions of CO₂ and NO_x were higher for the lower-higher molecular mass of alcohol-gasoline blends than those from pure gasoline fuel. Due to the lower heating values of methanol, ethanol, propanol, butanol and pentanol as compared to that of pure gasoline, brake power produced was lower than pure gasoline. The contribution of oxygen content presence in those alcohol fuels has improved the combustion process [25]; thus, reduced the exhaust emissions of CO and HC gases. The presence of oxygen content has also increased the thermal efficiency [26] for the fuel blends and resulted in the increased emissions of CO₂ and NO_x gases. This result can also be attributed to lower enthalpy of vaporization and higher flame speed of those alcohols than pure gasoline [27].

Table 1: Implications of heating value on alcohol-gasoline fuel

Performance Indices	Author(s)	Fuel blends	Output parameters	Results (vs baseline)	
Engine	S. Liu et al. [28]	MG (0-30% methanol)	Brake power, kW Brake torque, Nm BTE, %	Higher Lower Higher	
	M. Koc et al. [16]	EG (50%-85% of ethanol)	Brake torque, Nm Brake power, kW BSFC, g/kWh	Higher Higher Higher	
	Simeon Iliev [21]	MG (medium level of methanol) EG (medium level of ethanol)	Brake power, kW BSFC, g/kWh	Higher Higher	
				Lower Higher	
	Combustion behavior	B. Deng et al. [29]	BG (30 and 35% of ethanol)	Ignition timing, °CA Rate of heat release, 1/°CA Cylinder pressure, bar Cylinder temperature, °C	Higher Lower Lower Higher
				I. M. Yusri et al. [22]	2BG (5, 10 and 15% of 2-butanol)
Exhaust emissions		I. Gravalos et al. [24]	Blended (blend mixture)	CO, % CO ₂ , % HC, ppm NO _x , ppm	Lower Higher Lower Higher
	S. Altun et al. [30]			MG (low level methanol) EG (low level ethanol)	CO, % CO ₂ , % HC, ppm CO, % CO ₂ , % HC, ppm

Legends

Vs. baseline:	comparison with baseline fuel
MG:	Methanol-gasoline
EG:	Ethanol-gasoline
BG:	Butanol-gasoline
2BG:	2-butanol-gasoline
Blended:	Methanol, ethanol, propanol, butanol and pentanol-gasoline
Low level:	5 and 10% of ethanol
Medium level:	5%, 10%, 20%, 30%, and 50%
Blend mixture:	5 different blends with each alcohol percentage

S. Altun et al. [30] examined the effects of methanol and ethanol-gasoline blends with different percentage blends (5 and 10 vol.%) on emission characteristics of a spark-ignition engine. The engine was tested at varied engine speed between 1000 and 4000 rpm with intervals of 500 rpm. Average findings from the tests showed the emissions of CO and HC for methanol and ethanol-gasoline blends are lower than that of pure gasoline. Due to the oxygenated fuels of methanol and ethanol, M5 (methanol 5% - gasoline 95%), M10 (methanol 10% - gasoline 90%), E5 (ethanol 5% - gasoline 95%) and E10 (ethanol 10% - gasoline 90%) showed significant reduction on the emission of CO by 9%, 10.6%, 7% and 9.8%, respectively. The emission characteristics of HC were slightly the same as CO emission. In comparison between methanol and ethanol blends with pure gasoline fuel, M5 and M10 reduced the emissions of HC by 6.7% and 13%, while E5 and E10 decreased 5.3% and 15% of HC emissions. This condition has strengthened the idea of implementing alcohol as fuel blends to reduce hazardous exhaust emission resulted from engine combustion.

The literature survey revealed that limited studies have investigated the measurement of heating value of the fuel. These studies did not provide sufficient details about the used equipment, procedure of testing and the obtained data. Furthermore, most of these studies conducted depended on the results from the experimental measurements without any statistical analysis to evaluate the effect of increasing the percentage of fuel blend. The relation between higher and lower heating value is also important and should be considered during the analysis of the experimental data for more significant and reliable results.

Hence, in this research, application of alcohol blends on gasoline fuel has been thoroughly investigated with experimental and theoretical works using bomb calorimeter and statistical polynomial equations, respectively. The main task was to derive equations for the heating value properties of alcohol-gasoline blends using 10 different volumes percentages

(2.5, 5.0, 7.5, 10.0, 12.5, 15.0, 17.5, 20.0, 22.5 and 25.0 %). Variations of volume percentages (0-25%) were selected as it has been investigated as the optimal ranges of fuel blending for alcohol-gasoline blends [22, 26]. The polynomial equations with regressions were analysed to predict and observe the precision of each volume percentage selected. Validation of the results was then conducted by analysing the percentage error of each data.

Material and Equipment

Fuel Preparation

In this experimental study, methanol, ethanol and butanol have been blended with gasoline fuel at 2.5%, 5%, 7.5%, 10%, 12.5%, 15%, 17.5%, 20%, 22.5% and 25%. The blending processes were conducted using magnetic stirrer with continuous stirring at a temperature of 22-24°C to verify the homogeneity of the fuel blends [31]. Preparation must be done in a short period before starting the experiment to avoid separation process due to the higher latent heat of vaporization of the alcohol as shown in table 2. Besides that, alcohol fuels have higher octane number than that of gasoline fuel. Octane number is the main parameter to assess the anti-knock resistance [32]. The presence of oxygen molecule in alcohol fuel promotes a complete combustion process and reduces the hydrogen and carbon contents [33, 34].

Table 2: Properties of fuels [35-38]

Properties	Gasoline	Methanol	Ethanol	Iso-butanol
Molecular formula	C ₅ -C ₁₂	CH ₃ OH	C ₂ H ₅ OH	C ₄ H ₉ OH
Oxygen content (%)	0	49.9	34.7	21.6
Density (kg/m ³)	737	792	790	810
Octane number	95	109	108	90
Latent heat of vaporization	305	1103	840	716
Lower heating value (MJ/kg)	43.9	20.1	26.0	33.0

Experimental Setup

In the preparation of the fuel blends, proper experimental equipment and procedures were set up in a test room. The heating value of fuel was measured using IKA C 200 bomb calorimeter in accordance to ASTM-D240, DIN 51900 and ISO 1928.

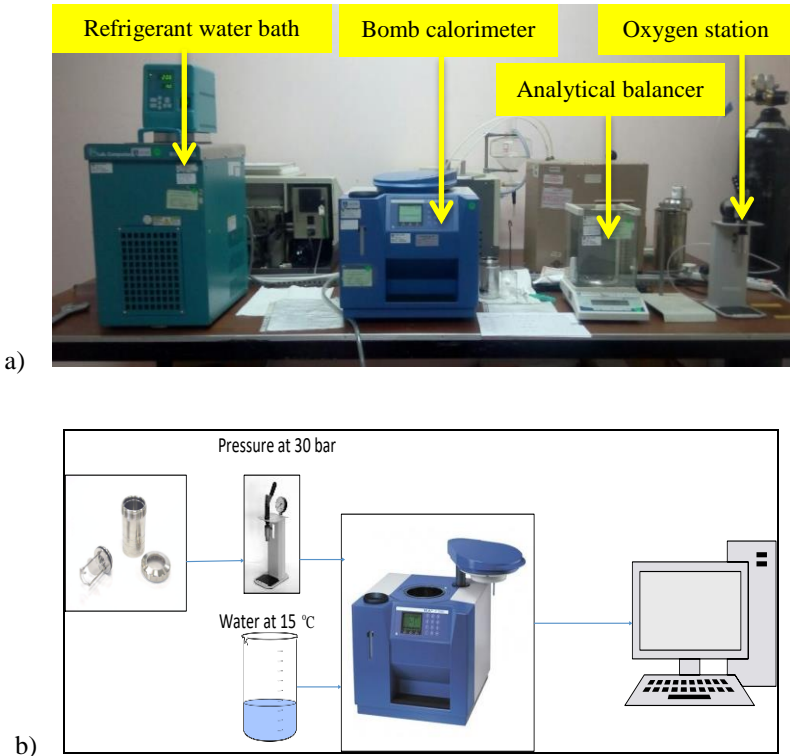


Fig. 1: Heating value test; (a) Experimental setup (b) Flowchart of the experiment

Figure 1(a) depicts the experimental setup of the heating value test which consists of refrigerant water bath, oxygen station, analytical balancer and bomb calorimeter. Refrigerant water bath was used to keep the water temperature at the initial value of 15°C. Each fuel blend sample was weighed using analytical balancer before being inserted into a high pressure vessel. The vessel was pressurized at 30 bar of oxygen gas for neat closure of the vessel lid. Figure 1(b) shows the process to perform the heating value experiment with analysis of data as the final process.

Data Analysis

Analysis of each fuel blend (methanol, ethanol and iso-butanol) data was conducted using the statistical polynomial equation of lower heating value against volume percentage of alcohol. The resulting polynomial equation was utilized to estimate the highest lower heating value of each alcohol-gasoline blend. Microsoft Excel 2010 was used for data analysis as well as the

calculation for predicting lower heating value at certain volume percentage. The highest order for the polynomial equation was two with the coefficient of determination; R^2 showing the best result suitable to predict the behaviour of lower heating value. Statistical polynomial equation was derived as below:

$$y = a_2x^2 + a_1x + a_0 \quad (5)$$

Which y = Response
 x = Correlated factor
 $a_0 \dots a_n$ = Coefficient of regression

Three parameters were used in this literature to analyse error and evaluate the heating values; average absolute error (AAE), average bias error (ABE) and coefficient of determination (R^2) [39]. The parameters are defined as follows:

AAE:

$$\frac{1}{n} \sum_{i=1}^n \left| \frac{h_e - h_m}{h_m} \right| \times 100\% \quad (6)$$

ABE:

$$\frac{1}{n} \sum_{i=1}^n \left(\frac{h_e - h_m}{h_m} \right) \times 100\% \quad (7)$$

R^2 :

$$1 - \frac{\sum_{i=1}^n (h_e - h_m)^2}{(\overline{h_m} - h_m)^2} \quad (8)$$

Which h_e = Estimated value of HHV
 h_m = Measured value of HHV
 $\overline{h_m}$ = Measured average value of HHV

Results and Discussions

Heating value of alcohol-gasoline blends

Heating value for alcohol-gasoline blends have been varied based on the type of alcohol and volume percentage of the blends. Figure 2 depicts the variations of heating value on volume percentage of alcohol, in which the overall result shows that iso-butanol-gasoline blends have the highest lower heating value at 2.5 vol.% with 44.16 MJ/kg than those of methanol and ethanol-gasoline blends. This is due to the higher heating value of iso-butanol (33.0 MJ/kg) compared to that of methanol and ethanol (20.1 and 26.0 respectively) as listed in table 2. Further blending of alcohols have reduced the lower heating value of pure gasoline with 44.23 MJ/kg as low as 0.158% for 2.5 vol.% of iso-butanol-gasoline blend which is due to the lower alcohol heating value compared to baseline gasoline. The highest result of lower

heating value for ethanol-gasoline blends were obtained at 2.5 vol.% with 43.96 MJ/kg. It is generally higher than overall vol.% of methanol-gasoline blends, in which the highest value of the latter was obtained at 5.0 vol.% with 43.03 MJ/kg.

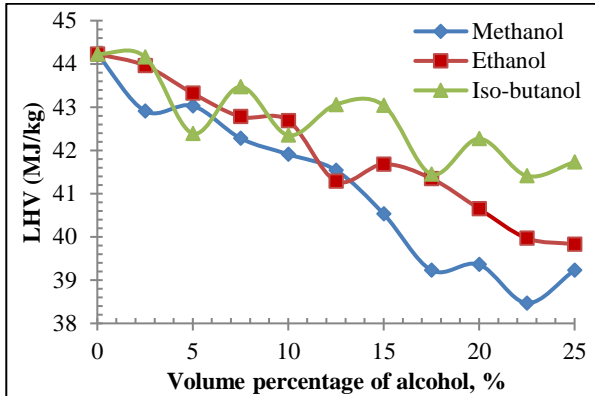


Fig. 2: LHV of alcohol-gasoline blends at different volume percentage, %

Several factors can be attributed to the results obtained such as the carbon chain of alcohol. Iso-butanol has higher carbon chain with four-carbon structures compared to those of methanol and ethanol which has one and two carbon structures, respectively [40]. Thus, with a larger number of carbon structure for iso-butanol, it enhances the energy content of gasoline-iso-butanol blends. Iso-butanol also offers another advantage over methanol and ethanol as it has lower heat of vaporization, as shown in table 2, to improve the cold-start condition of the engine [41].

Statistical polynomial equation with regressions

Polynomial equations from alcohol-gasoline blends were plotted in figure 3 (a, b and c). The equations were developed to correlate the heating value with volume percentage of alcohol-gasoline blends of 10 data for each set of alcohol blends and those correlations produced coefficient of determination, R^2 of above 0.5. Between those blends, iso-butanol-gasoline blends have the lowest R^2 with 0.692, compared to 0.9445 and 0.9691 for methanol and ethanol respectively. These values of R^2 were employed as a comprehensive parameter for the accuracy of the correlation.

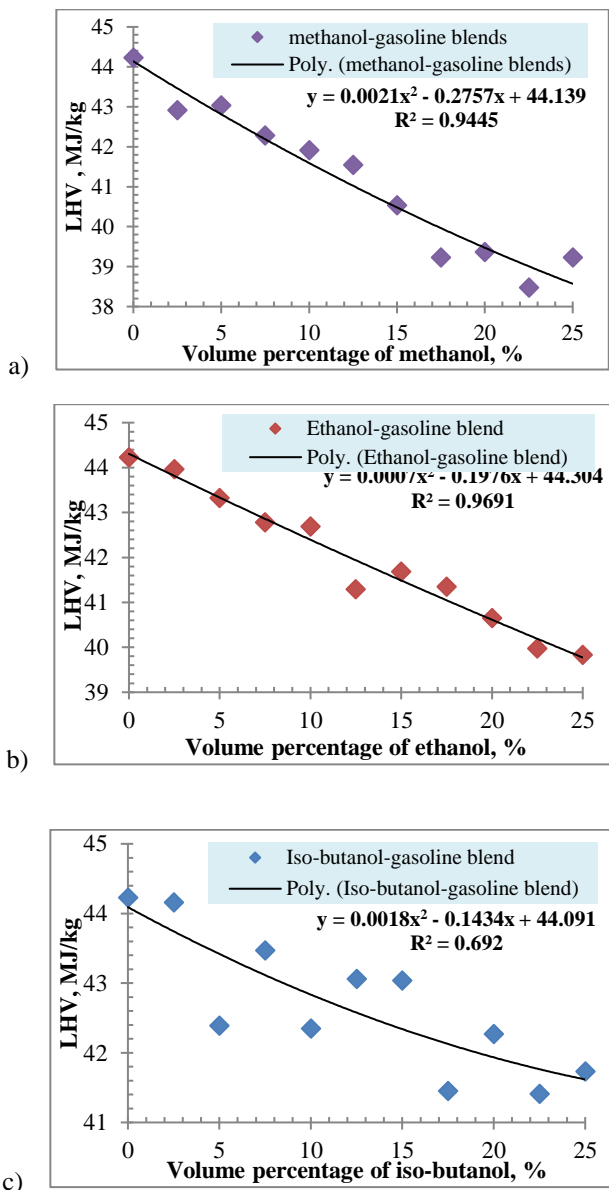


Fig. 3: Comparison of polynomial equation for LHV of (a) Methanol-gasoline, (b) Ethanol-gasoline and (c) Iso-butanol-gasoline blends

Validations of polynomial equations

After the derivation of estimation models for the heating value of alcohol-gasoline blends, average absolute errors (AAE) and average bias errors (ABE) were analysed at each model as in Table 3. These models exhibit higher accuracy of estimation methods in which the values of AAE were small. Thus, it shows that the bias of the correlation for these models was narrowed. In viewing the value of ABE, the positive value determines the overestimation of the response while the negative values show that the response was underestimated [42].

Table 3: Estimated model and statistic parameters for variations of alcohol-gasoline blends

Alcohol	a₂	a₁	a₀	R²	AAE, %	ABE, %
Methanol	0.0021	-0.2757	44.139	0.9445	0.9355	0.0021
Ethanol	0.0007	-0.1976	44.304	0.9691	0.438	0.014
Iso-butanol	0.0018	-0.1434	44.091	0.692	1.1604	0.0612

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Conclusions

In this study, estimation method of higher heating value properties on variation of alcohol-gasoline blends and volume percentage were suggested for the purpose of fuel blending selections. Comparison of estimated heating value with the measured heating value has been examined with the fundamental statistical parameters such as AAE, ABE and coefficient of determination, R². With high values of R² and low percentages of AAE and ABE for all derived models, a non-linear relationship has been suggested for heating value of each fuel blend according to statistical polynomial regressions with the highest order of two. Polynomial equations derived are expected to be highly accurate in estimating the blended fuel heating value as the coefficients of determination, R² obtained for the methanol, ethanol and iso-butanol blends were 0.9445, 0.9691 and 0.692, respectively. The estimation model is suggested to be used as it produces highly accurate and precise results for the alcohol-gasoline blends. This estimation method would help the researchers to easily obtain accurate and precise data for the heating value of alcohol-gasoline blends within the selected volume percentages which will be helpful in the studies of engine performance investigation.

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