

Phase behaviors and fuel properties of bio-oil-diesel-alcohol blends

P. Weerachanchai, C. Tangsathitkulchai, and M. Tangsathitkulchai

Abstract— Attempt was made to improve certain characteristics of bio-oil derived from palm kernel pyrolysis by blending it with diesel fuel and alcohols. Two types of alcohol, ethanol or butanol, was used as cosolvent to stabilize the phase of ternary systems. Phase behaviors and basic fuel properties of palm kernel bio-oil-diesel-alcohol systems were investigated in this study. Alcohol types showed a significant influence on the phase characteristics with palm kernel bio-oil-diesel-butanol system giving larger soluble area than that of palm kernel bio-oil-diesel-ethanol system. For fuel properties, blended fuels showed superior properties including lower values of density ($\sim 860 \text{ kg/m}^3$ at 25°C), viscosity ($\sim 4.12 \text{ mm}^2/\text{s}$ at 40°C), carbon residue (1.02-2.53 wt%), ash (0.018-0.034 wt%) and pour point (< -25 to -7°C), increased pH (~ 6.4) and giving reasonable heating values of 32.5-41.2 MJ/kg. To enable the prediction of some properties of fuel mixtures, the measured fuel properties including heating value, density, ash content and pH were fitted by Kay's mixing rule, whereas the viscosities of blended fuels at different temperatures were correlated by the modified Grunberg-Nissan equation and Andrade equation.

Keywords—Bio-oil, Fuel blend, Fuel properties, Phase behavior

I. INTRODUCTION

BIO MASS is known as a potential renewable energy source in satisfying environmental concerns. It has been utilized as an energy source through various conversion processes including direct combustion, gasification, pyrolysis, liquefaction and fermentation. However, biomass utilization in the form of liquid fuel is of particular interest due to its much higher energy density, ease of transport and reducing cost of handling. Bio-oil or pyrolysis liquid which is produced from biomass pyrolysis process has been considered as an alternative liquid fuel for both power generation and transport fuel [1], [2]. However, the direct use of bio-oil has certain disadvantages of possessing corrosive nature, high viscosity and its aging because of its containing a complex mixture of oxygenated compounds (from short chain organic compounds to polymer) [3].

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A large number of studies on bio-oil upgrading and/or using bio-oil in modified engines have been reported [3]. However, the simplest route to use bio-oil with the least modification of engines seems to be the use of a blend of bio-oil and diesel fuel [3]. It was reported that the addition of diesel can mitigate the problems due to acidity and high viscosity and the emulsions containing up to 10% bio-oil could be used [4]. However, bio-oil that has high amount of polar chemicals (acids, phenols, ethers, ketones, aldehydes and ester) is immiscible with non polar hydrocarbons of diesel (paraffin, naphtha and aromatic). Thus, to stabilize a homogeneous phase of bio-oil-diesel blend, an additive is obviously required. CANMET surfactant has been known as the most effective additive to stabilize bio-oil in diesel emulsion. It provides the stabilized homogenous phase of bio-oil-diesel mixture for longer time among other surfactants [4], [5]. Nevertheless, bio-oils produced from different biomass type and/or different process conditions have varied characteristics and this complicates the selection of a suitable additive for a specific bio-oil-diesel emulsion. In this regard, a more simple approach such as the use of a cosolvent to induce a more stable phase of the bio-oil-diesel mixture could be a promising alternative.

Alcohols have been considered as an alternative renewable fuel. When mixed with diesel, alcohols are known to alleviate some drawbacks of diesel fuel such as reducing black smoke and emissions of CO and NO_x [6]. The alcohol content of up to 20% in diesel can be used in IC engines without modification [6]. It was found that methanol and ethanol offered longer ignition delay period of combustion due to their higher latent heat of vaporization compared to that of diesel. In addition, isobutanol having similar latent heat of vaporization with added advantages of full miscibility in diesel and higher calorific value provides greater combustion characteristic in diesel engines [6]. Mixing alcohol with bio-oil has been reported to improve the undesired characteristics of bio-oil concerning heating value, viscosity and acidity [7], [8]. Also, it was noticed that solvent addition can prevent the bio-oil from aging effects [8], [9]. On combustion tests, bio-oil blended with ethanol gave shorter, wider and brighter flame but poorer atomization than those of diesel fuel when performing in a circular jet spray at atmosphere pressure [7].

As previously mentioned, the use of alcohol blended with bio-oil and diesel may provide a solution for its phase stability

and elimination of their shortcoming characteristics. However, detailed study of this three component system for application as a conventional fuel is relatively scarce. Thus, it is logical to study the phase stability and its basic fuel properties in this work. Palm kernel bio-oil was selected as a representative bio-oil for this study because it showed the most promising bio-oil among others in our previous study [10]. It gave the highest heating value (~ 40 MJ/kg), lowest acidity (pH ~ 5.8) and the closest boiling range distribution to that of diesel. In the present study, two types of absolute alcohol including ethanol and n-butanol were used to investigate the effect of solvent type on the phase behavior. These alcohols were chosen as they can be readily produced from renewable resource by fermentation of sugar and starch. The important fuel properties of blended fuels covering both the binary and ternary systems (palm kernel bio-oil-alcohol and palm kernel bio-oil-diesel-alcohol) were also investigated. In addition, to arrive at correlations for estimating some physical properties of fuel blends, the measured values of their fuel properties were fitted with equations from Kay's mixing rules, modified Grunberg-Nissan equation and Andrade equation.

II. EXPERIMENTAL

A. Materials

Palm kernel bio-oil was obtained from the slow pyrolysis of palm kernel cake in a tubular fixed bed reactor at 700 °C with a heating rate of 20 °C/min and N_2 flow rate of 200 °C/min. The derived bio-oil showed two separated phases of organic aqueous phase and oil phase. The upper aqueous phase was removed by decanting and the oil phase was kept for further study. Commercial diesel fuel (Delta-X Euro III) was purchased from Petroleum Authority of Thailand Public Company Limited (PTT) and analytical grade of ethanol (99.8%) and n-butanol (98.0%) used were acquired from Carlo Erba, Co., Ltd and Sigma-Aldrich Co. Ltd, respectively

B. Phase behaviors of ternary mixtures

Ternary phase behaviors were investigated by blending three components of bio-oil, diesel and alcohols (ethanol or butanol) at room temperature. Mutual solubilities of a two component systems consisting of bio-oil-diesel, bio-oil-alcohol, diesel-alcohol were preliminarily examined. For the three component systems, the phase behavior studies were performed by blending various volume fractions of bio-oil and diesel with successive increasing amount of an alcohol until a homogeneous mixture was visually observed. Phase stabilities of the homogeneous mixed samples were further ascertained by centrifugation at the speed of 3000 rpm for 20 min and the homogeneity of the mixtures was again decided by visual observation. In case of an opaque dark sample, a laser beam was allowed to pass through the sample to assist in this observation process. The blend compositions that gave a homogeneous phase characteristic after centrifugation were plotted on a solubility phase diagram.

C. Fuel properties

Palm kernel bio-oil, diesel, alcohols and blended fuels were characterized for their basic fuel properties including boiling range distribution (ASTM D86-96), calorific value (ASTM D240-92), flash point (ASTM D93-97), pour point (ASTM D97-96a), density (Gay-Lussac bottle), viscosity (ASTM D445-96), carbon residue (ASTM D524-97) ash content (ASTM D482-95) and acidity (744 pH meter, Metrohm).

III. RESULTS AND DISCUSSION

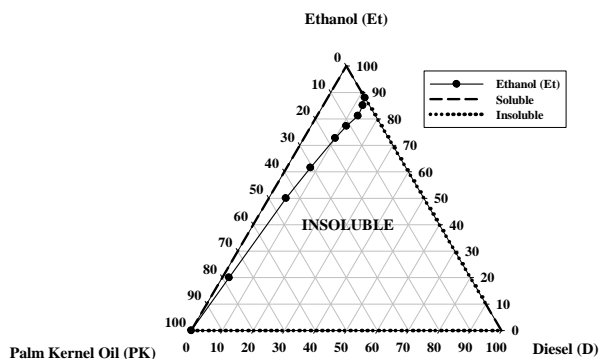
A. Phase behaviors of palm kernel bio-oil-diesel-alcohol systems

Palm kernel bio-oil-diesel blends did not give a homogeneous phase at any blend compositions. However, the diesel oil could be temporarily dispersed in a continuous phase of bio-oil at less than 10 vol% of diesel before the phase separation finally took place. It was observed that the color of diesel phase was changed from transparent yellow to dark red brown indicating the dissolution of some chemical components of bio-oil into diesel fuel. Moreover, darker color of diesel was observed with increased composition of bio-oil in the mixture.

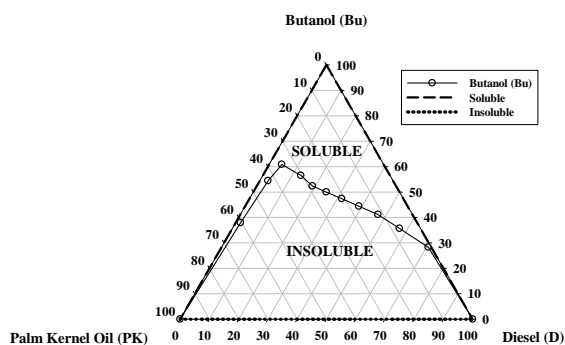
For the solubilities of bio-oil in alcohols, bio-oil is fully soluble in ethanol and butanol. The complete phase dissolution should result from the polar characteristic of palm kernel bio-oil containing high amount of polar molecules including 14.2 wt% of alcohols and phenols, 14.8 wt% of fatty acids, 7.2 wt% of ketones and aldehydes and 14.9 wt% esters [10]. For solubility of alcohols in diesel, it was found that ethanol showed partial miscibility in diesel, with either less than 10 vol% or greater than 88 vol% of diesel offering the single phase solutions. However, due to the longer chain of aliphatic hydrocarbon in butanol, a complete solubility of butanol-diesel mixture was observed at all proportions.

Figs. 1 (a) and (b) show ternary phase diagrams derived from the two types of alcohol for palm kernel bio-oil-diesel-alcohol system. It indicates that soluble characteristics of the two ternary systems are somewhat different. The soluble area of bio-oil-diesel-butanol system is much greater than that of bio-oil-diesel-ethanol system. This means that larger amount of ethanol is required to stabilize a single phase at the same composition of bio-oil-diesel. Using butanol as a cosolvent gave better miscibility at high content of diesel, while the single stable phase of bio-oil-diesel-ethanol mixture could be achieved only at the diesel content of less than 12.8 vol%. In addition, larger amount of butanol was required at high bio-oil content than at high diesel content indicating that butanol is better miscible in diesel than in bio-oil. Therefore, it may be addressed that alcohol type is a determining parameter on the phase behavior of ternary systems. It should be expected that if longer chain of aliphatic alcohol is employed to stabilize a ternary system, higher amount of alcohol will be required for a fuel mixture containing high composition of bio-oil than with high content of diesel.

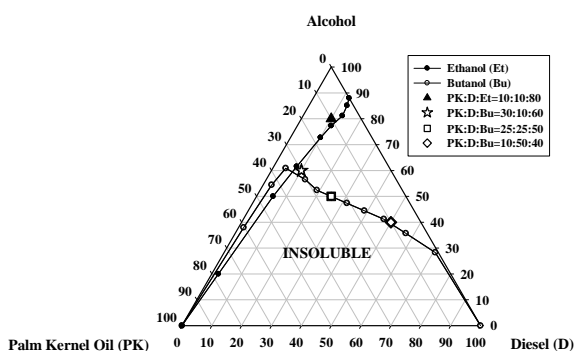
To reduce the amount of alcohol required, the miscibility of the fuel blend was assisted by mild heating at 60°C for 5 hr. A composition of the mixtures which is close to the true solubility line (40 vol% bio-oil, 10 vol% diesel and 50 vol% ethanol or butanol) was selected for this purpose. However, it was found that it was not able to maintain the stable phase of the system by this thermal treatment.



(a) Palm kernel bio-oil-Diesel-Ethanol



(b) Palm kernel bio-oil-Diesel-Butanol



(c) Palm kernel bio-oil-Diesel-Alcohol

Fig.1 Phase behavior of three component system

B. Fuel properties of fuel blends

Although palm kernel bio-oil possesses the properties of high calorific value (39.5 MJ/kg) and low acidity (pH ~ 5.9) among other bio-oils [10], it has some drawbacks such as high values of viscosity (58.7 mm²/s), carbon residue (6.3 wt%) and ash (0.063 wt%) and these characteristics may cause an adverse effect on the atomization quality, fuel droplet size and penetration in the combustion engines [7], [8]. To study the

possibility of using the upgraded bio-oil derived by blending with diesel and alcohol as alternative fuels, their basic fuel properties were thus investigated. The blends of bio-oil-ethanol, bio-oil-butanol and four compositions of bio-oil-diesel-alcohol fuels (as shown in Fig. 1 (c)) were selected for this study.

The fuel properties of the four primary fuels and various types of mixed fuels are shown in Table I. Blending of bio-oil (50 wt%) with ethanol or butanol (50 wt%) provided the advantageous properties of lowering the amounts of ash and carbon residue, reducing values of density, viscosity and pour point and giving slight increasing of pH. However, their heating value and flash point were lower compared to those of bio-oil. For the effect of alcohol type on the fuel properties, both ethanol and butanol gave similar fuel properties for the binary system (Table I). However, blending of bio-oil with ethanol gave superior properties of lowering in viscosity and pour point. The viscosity of 50 vol% ethanol blended with bio-oil (~ 4.3 mm²/s at 40°C) is comparable to that of commercial diesel fuel, whereas viscosity of butanol and bio-oil blend is higher with the value of about 9.2 mm²/s. The flash point of blended fuel of bio-oil and ethanol is relatively low, thus increasing the likelihood of self ignition during storage. On the other hand, the blend of bio-oil-butanol offers better properties of flash point and heating value for the similar compositions. Therefore, using the blended fuels of bio-oil-alcohol gives a benefit to cold flow operability but the safety during storage should be of concern.

For ternary system of bio-oil-diesel-alcohol, alcohol composition had a significant influence on their heating values. Because of the requirement for high alcohol content to keep the phase stable, the heating value of bio-oil-diesel-ethanol at the ratio of 10:10:80 by vol% was therefore closer to that of ethanol. Using butanol as a cosolvent gave relatively high calorific value in the range of 37.2-41.2 MJ/kg at the butanol contents of 40-60 vol%. In addition, alcohol type had the effect on flash point and pour point in the ternary blended fuels. The various compositions of using butanol as a cosolvent gave relatively constant values of flash point and pour point at 40 °C and -7 °C, respectively, whereas those properties were 19 °C and less than -25 °C when using ethanol at 80 vol%. Increasing content of bio-oil affected directly the amounts of carbon residue, viscosity and ash content in the blended fuels. The viscosities of these blended fuels are comparable to that of diesel fuel, whereas the ash content and the amount of carbon residue are slightly higher than those of diesel. However, a slight effect of fuel composition on the acidity and density was noted; pH is in the range of 6.2-6.5 and density is around 860 kg/m³ at 25°C.

Fig. 2 shows the boiling range distributions derived from various types of fuel blends. It is noticed that bio-oil gave the boiling distribution curve closest to that of diesel fuel but its high carbon residue content limited the maximum volume of distillate to 70 vol%. Blending of alcohol in bio-oil can reduce the carbon residue content in the fuel blends (Table I) and the mixture of bio-oil-butanol (50:50 by vol%) provided wider distillation range up to 88% of distillate volume. For the three components system, the range of boiling distribution could be extended to more than 90 vol%. Bio-oil-diesel-

ethanol fuel with composition 10:10:80 by vol% showed a complete distillation curve. However, its boiling curve was lowest, showing three steps of distillation range with the lowest initial and final boiling point being at 74 °C and 268 °C, respectively. For the mixtures of bio-oil-diesel-butanol, their initial boiling points were about 95 °C but their final boiling points depended on the compositions of fuel. The highest final boiling point was attained for the fuel blends containing highest fraction of diesel (PK:D:Bu=10:50:40 by vol%). Nevertheless, its final boiling point was lower than that of diesel fuel (338 °C for blended fuel versus 378 °C for diesel). This may be an advantageous characteristic of the fuel blend because it can provide the lower smoke and exhaust emissions [7], [11]. Moreover, lower initial boiling points derived from the presence of alcohol in the blends could give the better properties of cold-starting and warming-up than those of diesel fuel [11]. As to the effect of fuel composition, the higher diesel content in the bio-oil-diesel-butanol mixture showed the marked rising of the distillation curve after the complete distillation of butanol. This is also noticed from the distillation curve of the blended fuel consisting only of diesel and butanol (50:50 by vol%). It should be noted that the large difference of distillation temperature between 10 vol% and 80 vol% (190 °C) derived from the blends of PK-10:D-50:Bu-40 and D-50:Bu-50 compared with that of conventional diesel fuel (125 °C) could result in longer warming-up time for the engines [11]. On the other hand, higher bio-oil content in the blends (PK:D:Bu=25:25:50 and 30:10:60 by vol%) showed a gradual increase of distillation temperature, thus giving smaller difference of distillation temperature between 10 vol% and 80 vol% in comparison with diesel (140 °C). However, complete distillation was not obtained (94 vol% distilled) with the mixtures containing high bio-oil content.

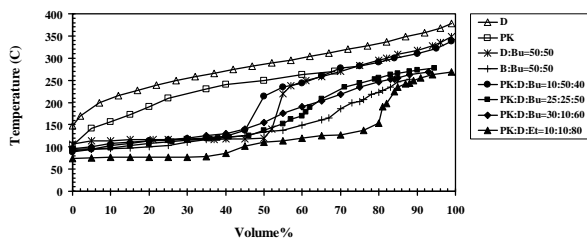


Fig. 2 Distillation curves of fuel blends (Palm kernel bio-oil (PK), Diesel (D), Ethanol (Et) and Butanol (Bu))

C. Prediction of basic fuel properties in binary and ternary fuel blends

To predict fuel properties of fuel blends from the corresponding properties of their compositions, the measured values of fuel properties were checked with the mixing rule. Kay's mixing rule has been used as the simple approach for predicting the physical properties in the hydrocarbon industry [12] and presented as (1)

$$\varphi_B = \sum_i^n x_i \varphi_i \quad (1)$$

where φ_B is a property of the blend, φ_i is corresponding property of pure i component and x_i is mole fraction. The agreement of the measured values and the values derived from Kay's mixing rule was determined by the value of absolute average deviation (AAD), defined as (2)

$$AAD = \frac{100}{NP} \sum_i^n \left| \frac{\varphi_{Exp} - \varphi_{Cal}}{\varphi_{Exp}} \right| \quad (2)$$

where NP is the number of experiment data, φ_{Exp} is the experimental value of the property and φ_{Cal} is the predicted value of the property.

In this work, it was found that Kay's mixing rule could be applied for some properties of binary systems (Fig. 3). Heating value, pH and ash content could be approximated by Kay's mixing rule by using mass fraction instead of mole fraction. The using of mass fraction in (1) gave a little less AAD than that of using volume fraction. The mean of AAD calculated by mass fraction for heating value, pH and ash content were 1.76%, 1.04% and 15%, respectively, whereas those calculated based on volume fraction were 2.58%, 1.91% and 19.4%, respectively. However, the computation based on using volume fraction works well for the density of the mixtures (1.37%AAD for volume fraction but 3.33%AAD for mass fraction). In addition, applying Kay's mixing rule for the ternary mixtures was found to be satisfactory for heating value, pH and density with the maximum AAD being about 3.9%, whereas that of ash content is relatively high of 42.7%. However, the calculations of some properties such as viscosity, flash point and pour point were not compatible with those estimated from Kay's mixing rule. It has been reported in the work of Joshi and Pegg [13] that the measured values of

TABLE I
FUEL PROPERTIES OF BLENDING FUELS

Chemical	Calorific value (MJ/kg)	Density @ 25°C (kg/m ³)	Viscosity @ 40°C (mm ² /s)	pH	Ramsbottom carbon residue (wt%)	Ash (wt%)	Flash point (°C)	Pour point (°C)
Palm kernel bio-oil (PK)	39.5	1,120	58.7	5.87	6.32	0.063	82	1
Diesel (D)	44.5	844	3.69	-	0.060	0.018	78	-10
Ethanol (Et)	28.7	793	1.22	6.58	0.021	-	14	-114.1 ^a
Butanol (Bu)	33.4	810	2.43	6.70	0.027	-	34	-89.5 ^a
PK-50:Et-50	35.2	960	4.31	6.11	4.66	0.034	21	-19
PK-50:Bu-50	37.1	946	9.21	6.18	4.20	0.039	42	-7
D-10:Et-90	30.9	793	1.35	6.63	-	-	17	<-25
D-90:Et-10	41.9	829	3.22	6.66	-	0.018	21	-11.5
D-50:Bu-50	39.8	820	2.58	6.65	-	0.013	42	-10
PK-10:D-10:Et-80	32.5	834	1.77	6.46	1.02	0.018	19	<-25
PK-10:D-50:Bu-40	41.2	838	3.53	6.54	1.12	0.016	40	-8.5
PK-25:D-25:Bu-50	39.3	876	5.30	6.21	2.16	0.034	40	-6
PK-30:D-10:Bu-60	37.2	891	5.86	6.24	2.53	0.031	41	-7

^a freezing point

pour point were more consistent by applying an empirical second-order polynomial equation than using a linear equation for biodiesel-diesel blends.

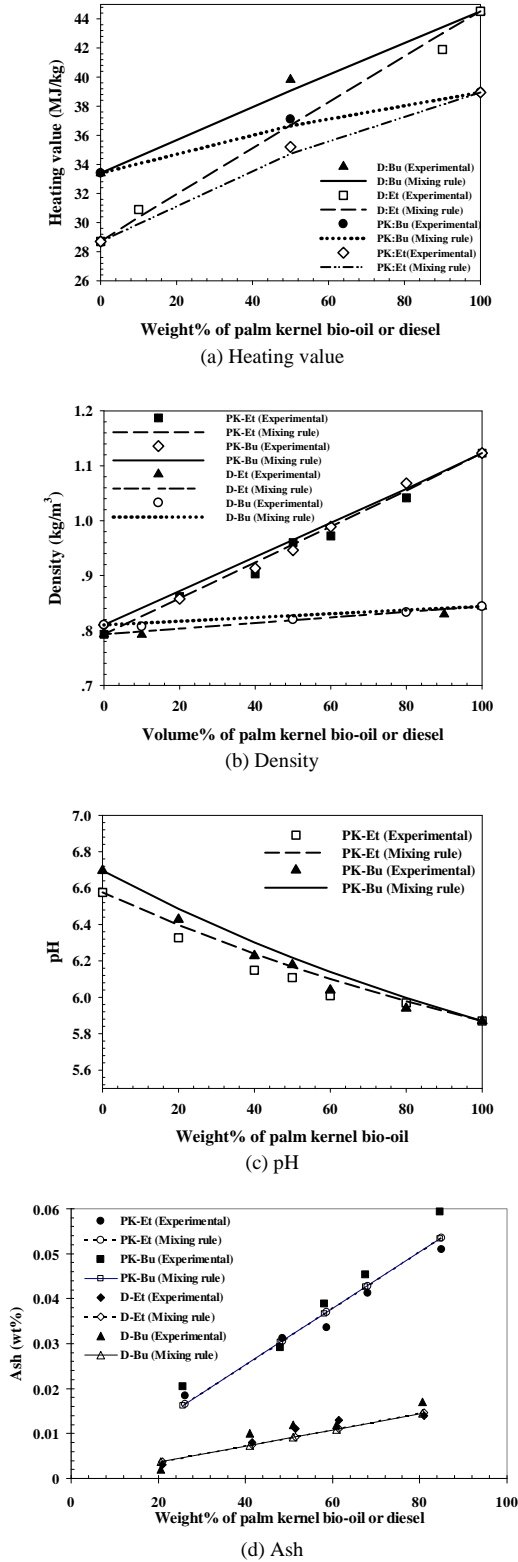


Fig. 3 Fuel properties of blending fuels compared with calculation by mixing rule (Palm kernel bio-oil (PK), Diesel (D), Ethanol (Et) and Butanol (Bu))

D. Viscosity estimation of binary and ternary fuel blends

In this work, the kinematic viscosities of pure components and the blends derived from various compositions of bio-oil-alcohol, diesel-alcohol and bio-oil-diesel-alcohol were measured as a function of temperature.

For predicting viscosity of the blend, there are several correlation equations that have been proposed but the Grunberg-Nissan equation is most commonly used [12] and is expressed as (3)

$$\ln \mu_B = \sum_i^n x_i \ln \mu_i + \sum_i^n \sum_j^n x_i x_j G_{ij} \quad (3)$$

where μ_B is the dynamic viscosity of blend (mPa·s), μ_i is the dynamic viscosity of pure i component (mPa·s), x_i is the mole fraction and G_{ij} is the interaction parameter, $G_{ij}=0$ for $i=j$.

However, since the kinematic viscosity was experimentally measured, it is more convenient to employ the volume fraction along with kinematic viscosity in (3) instead of mole fraction and dynamic viscosity, (3) now becomes

$$\ln \eta_B = \sum_i^n v_i \ln \eta_i + \sum_i^n \sum_j^n v_i v_j G_{ij} \quad (4)$$

where η_B is the kinematic viscosity of blend (mm^2/s), η_i is the kinematic viscosity of pure i component (mm^2/s), v_i is the volume fraction and G_{ij} is the interaction parameter, $G_{ij}=0$ for $i=j$.

As to the effect of temperature on viscosity, the commonly recommended equation is Andrade equation [12] and is represented by (5)

$$\eta = e^{(A+B/T+C/T^2)} \quad (5)$$

where η is the kinematic viscosity (mm^2/s), T is the absolute temperature (K) and A , B and C are constants for the fluid.

Firstly, to explain the viscosity-temperature characteristics of pure component fuels including bio-oil, diesel, ethanol and butanol, their measured viscosities were fitted by Andrade equation. Fig. 4 indicates that the viscosities of the pure components decreased non-linearly with increasing temperature. It is also found that the component having higher viscosities showed a more drastic decrease with increasing temperature. The viscosity-temperature characteristics of these primary fuels were found to correlate well with the Andrade equation with constants A , B and C shown in Table II and the average regression coefficient (R^2) was 0.99954.

On the viscosities of the blended fuels, the interaction parameters (G_{ij}) for the blends of bio-oil-ethanol, bio-oil-butanol, diesel-ethanol and diesel-butanol were determined by fitting the viscosity data with the modified Grunberg-Nissan equation (4). The viscosities were also correlated by the modified Grunberg-Nissan equation without the effect interaction parameters ($G_{ij}=0$), the equation is shown as in (6)

$$\ln \eta_B = \sum_i^n v_i \ln \eta_i \quad (6)$$

