DEVELOPMENT OF WRIGHT BLENDING METHOD IN VISCOSITY ESTIMATION OF LIQUID-BINARY MIXTURE OF BASE OIL AND OLEFIN COPOLYMERS (OCPs)

Nelson Saksono[1)], **Subiyanto**[2)], and **Setyo Widodo**[2)]
[1)]Lecturer of Chemical Engineering Department – University of Indonesia
[2)]Researcher at "LEMIGAS" R & D Centre for Oil and Gas Technology
Jl. Ciledug Raya, Kav. 109, Cipulir, Kebayoran Lama, P.O. Box 1089/JKT, Jakarta Selatan 12230 INDONESIA
Tromol Pos: 6022/KBYB-Jakarta 12120, Telephone: 62-21-7394422, Faxsimile: 62-21-7246150
nelson@che.ui.ac.id

First Registered on February 18th, 2011; Received after Corection on March 9th, 2011
Publication Approval on : May 31st, 2011

ABSTRACT

This study aims to develop mathematical equations used in Wright's method to predict kinematic viscosity of liquid-binary mixture consisting of base oil and additive. The equation is developed by addition of specific constants (α_i and α_c), representing interaction of each component in the mixtures. Evaluation is done using 70 empirical data from 35 samples derived from liquid blending of 4 types of base oils (B.1, B.2, B.3 and B.4) and olefin copolymers (OCPs), varied in the range of 5-30 % of weight. Kinematic viscosity is measured at 40°C and 100°C using a cannon automatic viscometer series 2000 (CAV 2000) according to ASTM method D 445. Validation of the equation (Developed-Wright's method) is performed over all of liquid-binary mixtures of base oil-OCPs, and the accuracy is indicated by percent average absolute deviation (%AAD). The results show that the addition of specific constants could minimize the deviations of estimated values. The average deviation of Developed-Wright's method on kinematic viscosity estimation at 40°C and 100°C becomes 2.056 % and 1.917% respectively, lower than Wright's method which are 8.341 % and 14.696%; meanwhile the maximum deviation reaches 5.821 % and 4.657%, lower than Wright's method which are 21.256 % and 25.265% respectively. These values indicate that the Developed-Wright's method has better accuracy.

Keywords: *Developed-Wright's method, kinematic viscosity, base oil, olefin copolymers (OCPs)*

I. INTRODUCTION

Lubricating oil is liquid lubricant whose main function is to prevent friction, wear and surface damage in machinery system, such as gears and bearings. Lubricating oil also serves to prevent corrosion, transfer heat, and disperse dirt or wear particles (Freeman, 1962; O'Connor and Boyd, 1968; Fein, 1992; Booser, 1996; and Wartawan, 1998). Lubricating oils used by consumers are produced from base oil and additives about 5-30 % by weight (Srinivasan, *et al.*, 2007). Olefin copolymers (OCPs) are additive having a large concentration used as viscosity index improver in lubricating oil formula. Lubricating oil production is carried out by several stages of estimation and formulation in laboratory scale, followed by commercial-scale production. Estimation and formulation are important steps to ensure product quality in accordance with the quality specifications. Kinematic viscosity is the most important parameter in estimation and formulation step. The presence of OCPs as additive which exhibit strong non-Newtonian and thickening effect properties causes a large deviation in this step.

Several equations have been proposed to facilitate viscosity estimation of multi-component mixtures, such as Rahmes and Nelson (1948), Sovilj (1995), Dias, R.M. *et al.* (1996), Valeri D. and Meirelles (1997), Abu-Eishah (1999) and Bair, S. *et al.*, (2001). The equation proposed by J. de Guzman in 1913 showing the correlation of viscosity and temperature, known as the Andrade equation (Viswanath, *et al*, 2007, p. 139). Most of the equations used to estimate binary or multi component liquid-mixture are developed based on empirical data, such as Arrhenius (1887), Kendall and Monroe (1917), Van Der Wyk (1936), Grunberg–Nissan (1949), and McAllister (1960) (Viswanath, *et al*, 2007, p. 427-432).

Several equations and methods on kinematic viscosity-estimation of petroleum and its derivatives mixtures are known, such as Wright's method (Wright, 1946), Refutas equation (Maples, 2000), and ASTM method (*Annual Book of ASTM Standard*, 2009). Preliminary research indicates that the Wright's method has better accuracy than others, as indicated by percent average absolute deviation (%AAD), about 10-15%. This study aims to develop Wright's method in kinematic viscosity estimation of liquid-binary mixtures involving base oil and OCPs which exhibit strong non-Newtonian properties. This new method is expected to reduce the cost of blending and laboratory tests on lubricating oil formulation.

II. DEVELOPMENT OF WRIGHT METHOD

A. Wright's Method

Estimation method proposed by W. A. Wright refers to viscosity-temperature correlation developed in Walther - MacCoull equation (eq. 1).

$$\text{Log.log}\, Z = A - B \log T \qquad \text{....... (1)}$$

The value $Z = (v + a + C - D + E - F + G - H)$, and the constant a H" 0.7 (Kurano *et al*, 1992). Lubricating oil formulation involves the kinematic viscosity > 2 mm²/s, so that C to H can be ignored.

Wright's method defines each component based on its fraction and kinematic viscosity at two temperatures measurements. Viscosity of component i at temperature T_{ij}, is v_{ij}, and the fraction as f_i.

$$Z_{ij} = v_{ij} + 0{,}7 + \exp(-1.47 - 1{,}84v_{ij} - 0{,}51v_{ij}) \qquad \text{... (2)}$$

$$W_{ij} = \log[\log(Z_{ij})] \qquad \text{....... (3)}$$

$$T_{ij} = \log[t_{ij} + 273.15] \qquad \text{....... (4)}$$

v_{ij} is the kinematic viscosity [mm²/s] of component i at temperature T_{ij} [°C]. Addition of an exponential (Eq. 2) can be ignored for liquid with kinematic viscosity value higher than 2 mm²/s. The equations are developed using the dimensionless transformation numbers of viscosity and temperature. The schematic concept of the Wright Blending Method is illustrated in Figure 1.

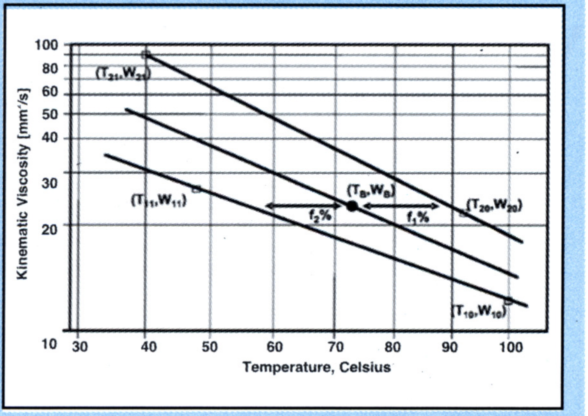

Figure 1
Schematic Illustration of Wright Blending Method
(*Annual Book of ASTM Standard,* 2009)

Curve gradient for component i (reciprocal-gradient of the viscosity-temperature curve, m_i^{-1}) and the predicted transformed viscosity (W_B) of the blend at temperature (T_B) can be calculated with Eq. 5 and Eq. 6, as follow:

$$m_i^{-1} = \frac{(T_{i1} - T_{io})}{(W_{i1} - W_{i0})} \qquad \text{....... (5)}$$

$$W_B = \frac{T_B + \sum fi(mi^{-1}W_{i0} - T_{i0})}{\sum (fi.mi^{-1})} \qquad \text{....... (6)}$$

dimensionless numbers are used to calculate the kinematic viscosity of the mixture with the following equation:

$$Z_B^{'} = 10^{W_B} \qquad \text{....... (7)}$$

$$Z_B = 10^{Z_B^{'}} - 0{,}7 \qquad \text{....... (8)}$$

$$v_B = Z_B - \exp[-0{,}7487 - 3{,}295Z_B + 0{,}6119Z_B^2 - 0{,}3193Z_B^3] \qquad \text{..... (9)}$$

Z'_B and Z_B are the results of intermediate calculation steps with no physical meaning. In estimation of viscosities between 0.12 - 1000 mm²/s, the transforming Eq. 2 and Eq. 3 and the un-transforming equations Eq. 8 and Eq. 9 have a discrepancy less than 0.0004 mm²/s (*Annual Book of ASTM Standard*, ASTM D 7152, 2009, p.3).

B. Development of Wright's Method

Lubricating oil formulations always involves materials with kinematic viscosity value higher than 2 mm²/s, so Eq. 2 and Eq. 9 can be simplified to:

$$Z_{ij} = v_{ij} + 0{,}7 \qquad \text{.......} \ (10)$$

$$v_B = Z_B \qquad \text{.......} \ (11)$$

where, Eq. 6 can be re-arranged into:

$$W_B = \frac{T_B}{\sum(fi.mi^{-1})} + \frac{\sum fi(mi^{-1}W_{i0} - T_{i0})}{\sum(fi.mi^{-1})}$$

$$W_B = m_B.T_B + C; where \ \ m_B = \frac{1}{\sum(fi.mi^{-1})} and$$

$$C = \frac{\sum fi(mi^{-1}W_{i0} - T_{i0})}{\sum(fi.mi^{-1})}$$

Deviation of Wright's method is indicated from the gradient and intercept of the curve (Figure 1). Re-arranging Eq. 6 results in reciprocal-gradient equation and intercept of the curve as follow:

$$m_B^{-1} = \sum(fi.mi^{-1}) \qquad \text{.......} \ (12)$$

$$C = \frac{\sum fi(mi^{-1}W_{i0} - T_{i0})}{m_B^{-1}} \qquad \text{.......} \ (13)$$

$$\frac{C}{m_B^{-1}} = \sum fi(mi^{-1}W_{i0} - T_{i0}) \qquad \text{.....} \ (14)$$

Empirical data indicate the deviation of reciprocal-gradient and intercept in Wright's method, so that:

$$(m_B^{-1})real \neq \sum(fi.mi^{-1}) and$$

$$\left(\frac{C}{m_B^{-1}}\right)real \neq \frac{\sum(fi.mi^{-1}W_{i0} - T_{i0})}{m_B^{-1}}$$

Preliminary study shows that deviations from the ideal curve change exponentially with concentration. Based on these phenomena, a new equation is proposed to modify Eq. 12 and Eq. 14 for a real mixture:

$$(m_B^{-1})real = \sum(fi^{\alpha_i}.mi^{-1}) \qquad \text{....} \ (15)$$

$$\left(\frac{C}{m_B^{-1}}\right)real = \sum fi^{\alpha_c}(mi^{-1}W_{i0} - T_{i0}) \qquad (16)$$

where, and are specific constants indicating specific interaction of component *i* and the mixture. Substitution of Eq. 14 and Eq. 15 into Eq. 6 gives a new equation, as follows:

$$W_B = \frac{T_B + \sum fi^{\alpha_c}(mi^{-1}W_{i0} - T_{i0})}{\sum(fi.mi^{-1})} \qquad \text{.......} \ (17)$$

III. MATERIALS AND METHOD

This study is conducted in five stages as described in Figure 2, i.e. i). Literature review; ii). Sample preparation and laboratory test; iii). Wright's method development; iv). Data evaluation and new equation validation; and v). Conclusion. Liquid-binary mixtures are prepared from base oils (B.1, B.2, B.3 and B.4) and OCPs, varied within 5-30 % by weight. A certain amount of base oils and additives are weighed and blended with OCPs at 70 ± 5 °C and stirred at 1500 ± 50 rpm for about 30 – 60 minutes.

Kinematic viscosity values are measured at 40°C and 100°C using automatic cannon viscometer series 2000 (CAV 2000) according to ASTM method D445

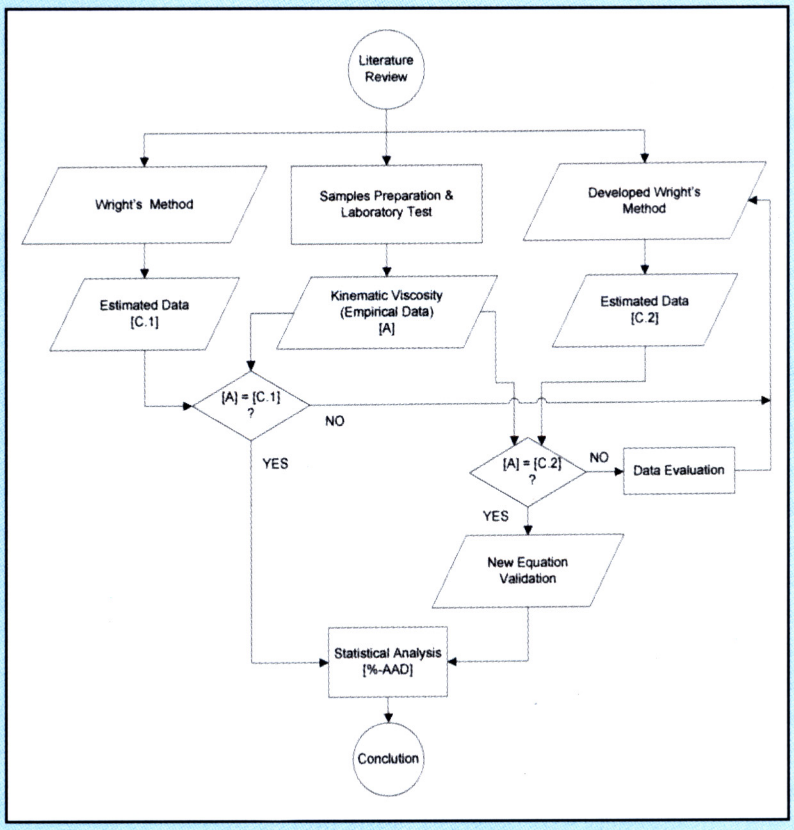

Figure 2
Method

2. Specific Constant Calculation for OCPs

The presences of OCPs which exhibits strong non-Newtonian properties change the components interaction on the mixtures. Correction of the reciprocal-gradient and intercept for liquid-binary mixture of base oil with OCPs are performed using known specific constant of the base oil ($a = 1$). Analysis and evaluation are conducted to 64 data from 32 samples of liquid-binary mixtures. The result shows that the development of Wright's method by adding a specific constants (a), as shown in Eq. 15 and Eq. 16, can minimize the deviation values of the reciprocal-gradient and intercept correction (Figgure 4 and Figure 5). The accuracy improves and it is indicated by

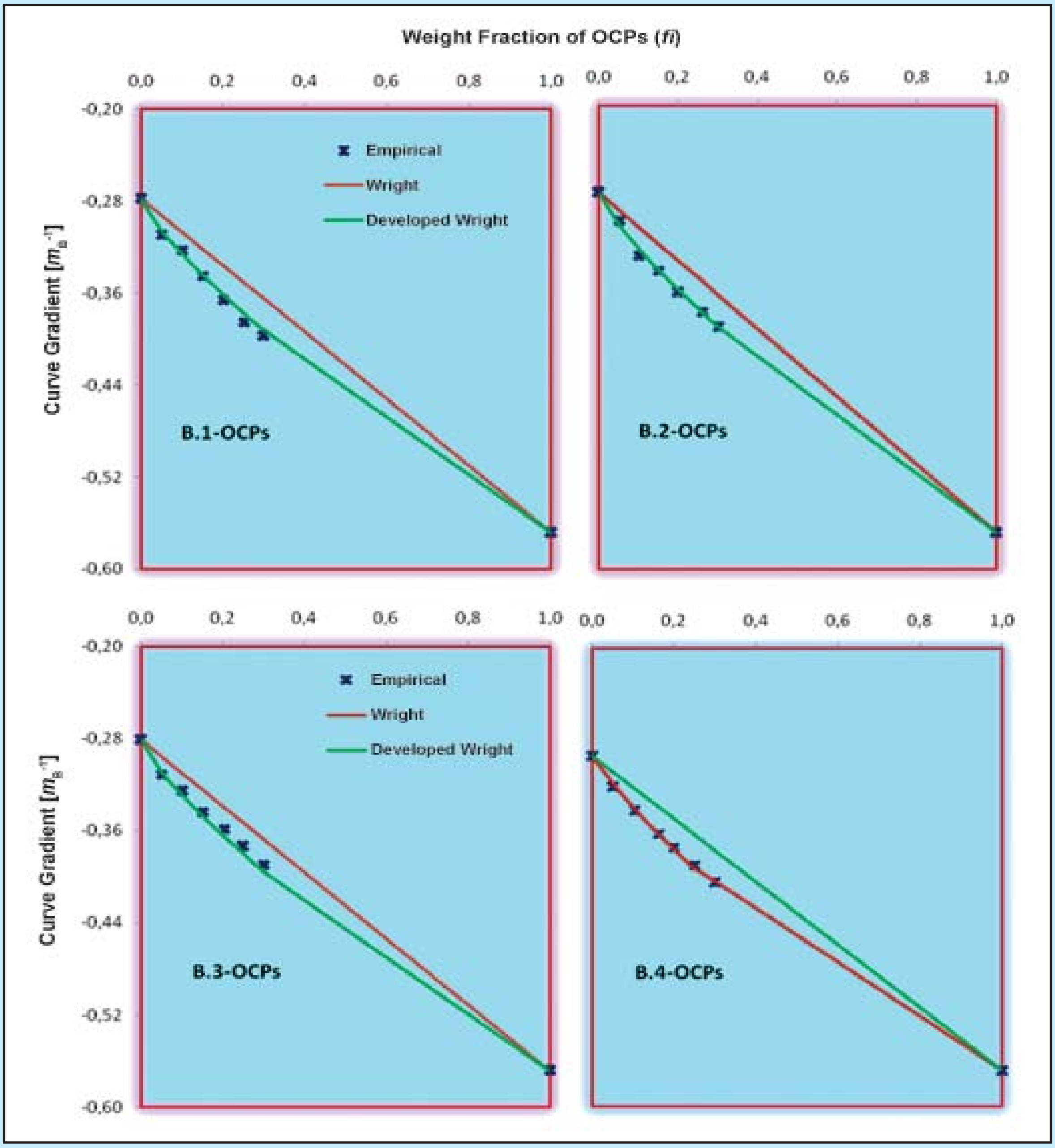

Figure 4
Reciprocal-gradient for liquid-binary mixture of Base oil - OCPs.
(*source: Author's data evaluation*)

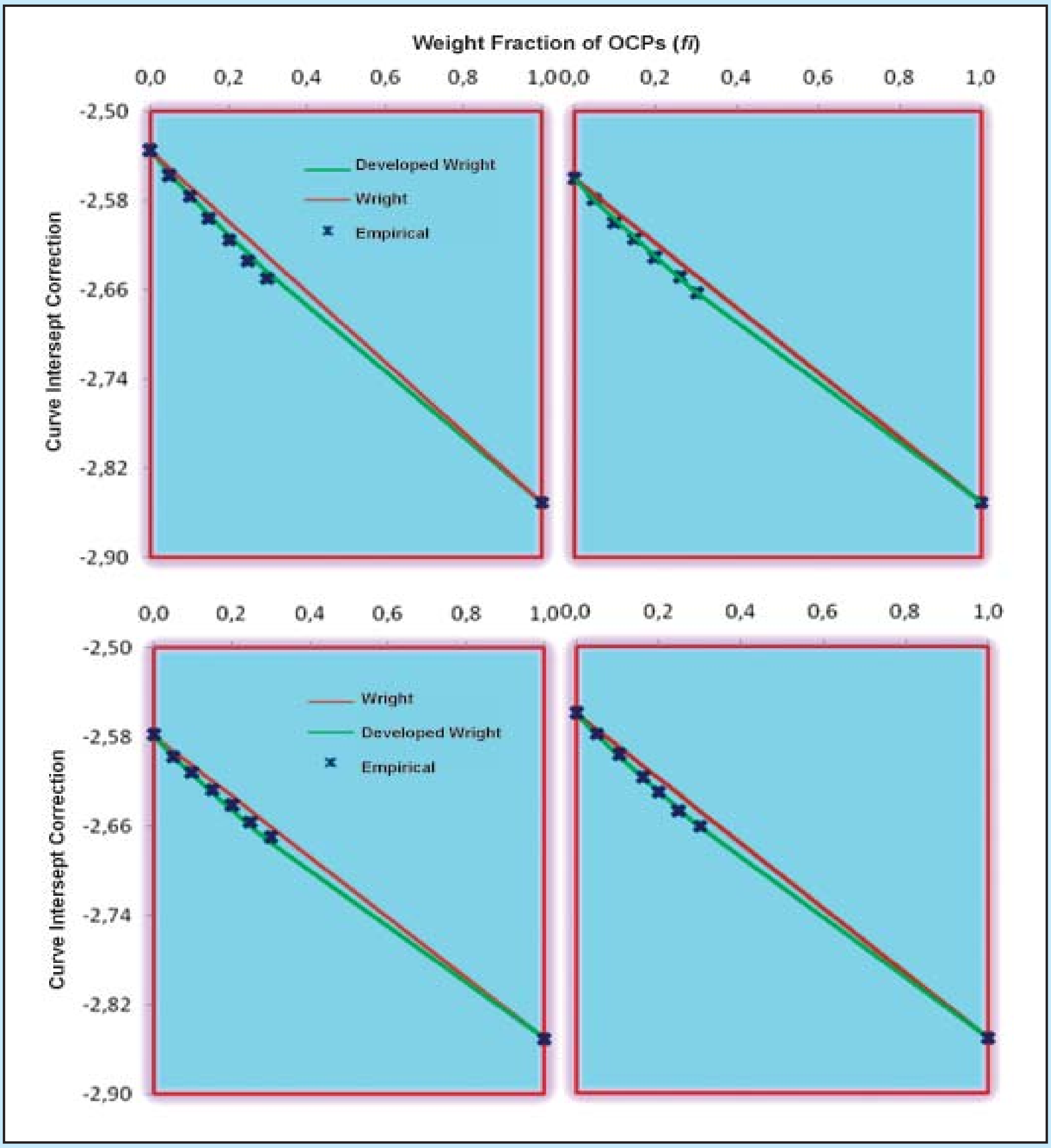

Figure 5
Intercept correction for liquid-binary mixture of Base oil - OCPs.
(*source: Author's data evaluation*)

the lower values of %AAD of reciprocal-gradient and intercept correction to 0.6822% and 0.0546% respectively. These values are lower than those derived from Wright's method (4.6741% and 0.3031%).

The empirical data also indicate that interaction parameters of OCPs in liquid-binary mixtures are depended on kinematic viscosity of base oils to be blended. Both of spe α_i and α_c) tend to rise with kinematic viscosity of base oil (Figure 6). Based on these results, a simple correlation could be formulated between specific constant and the average kinematic viscosity at two measured temperatures, as follow:

$$\alpha_i = 9.05 \ \ x\ 10^{-4}\ x\ \upsilon_{BO} + 0.848 \qquad \text{........ (19)}$$

$$\alpha_i = 1.26 \ \ x\ 10^{-4}\ x\ \upsilon_{BO} + 0.987 \qquad \text{........ (20)}$$

where, v_{BO} is average kinematic viscosity of base oil at two measured temperatures.

B. Validation of New Equation

Validation is conducted to determine the accuracy of new equation in kinematic viscosity prediction of 24 liquid-binary mixtures of base oils – OCPs, measured at 40°C and 100°C. Based on the above results, kinematic viscosity of liquid-binary mixtures of base oil-OCPs can be estimated using Eq.17.

$$WB = \frac{T_B + \Sigma f_i^{a_c}(m_i^{-1}W_{io} - T_{io}}{\Sigma\left(f^{a_i}_{\ i} . m_i^{-1}\right)}$$

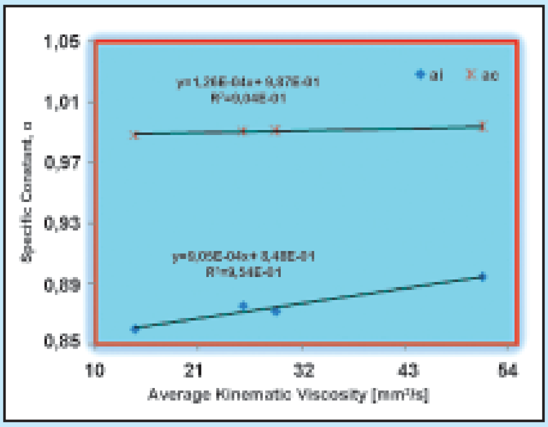

Figure 6
Correlation of specific constants with average kinematic viscosity of base oil
(*source: Author's data evaluation*)

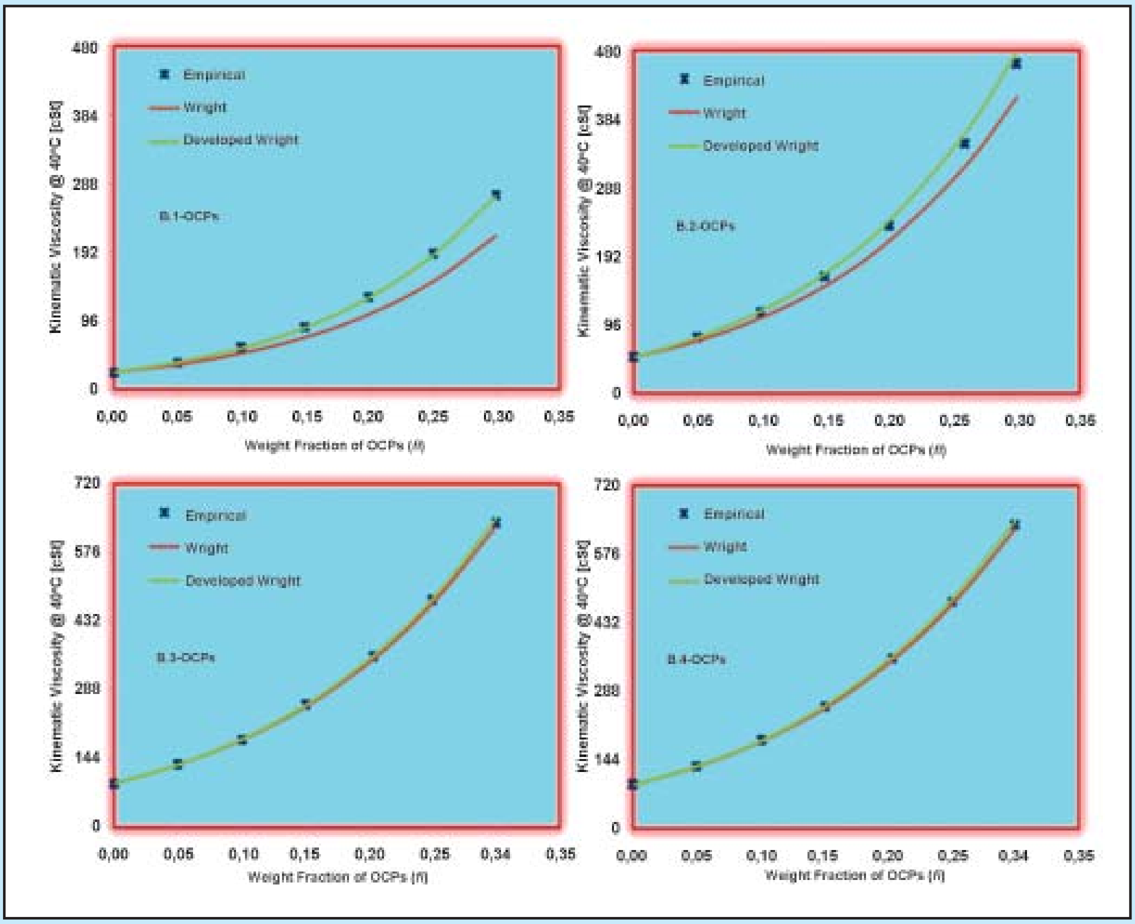

Figure 7
Kinematic viscosity of base oil-OCPs liquid-binary mixtures at 40°C.
(*source: Author's data evaluation*)

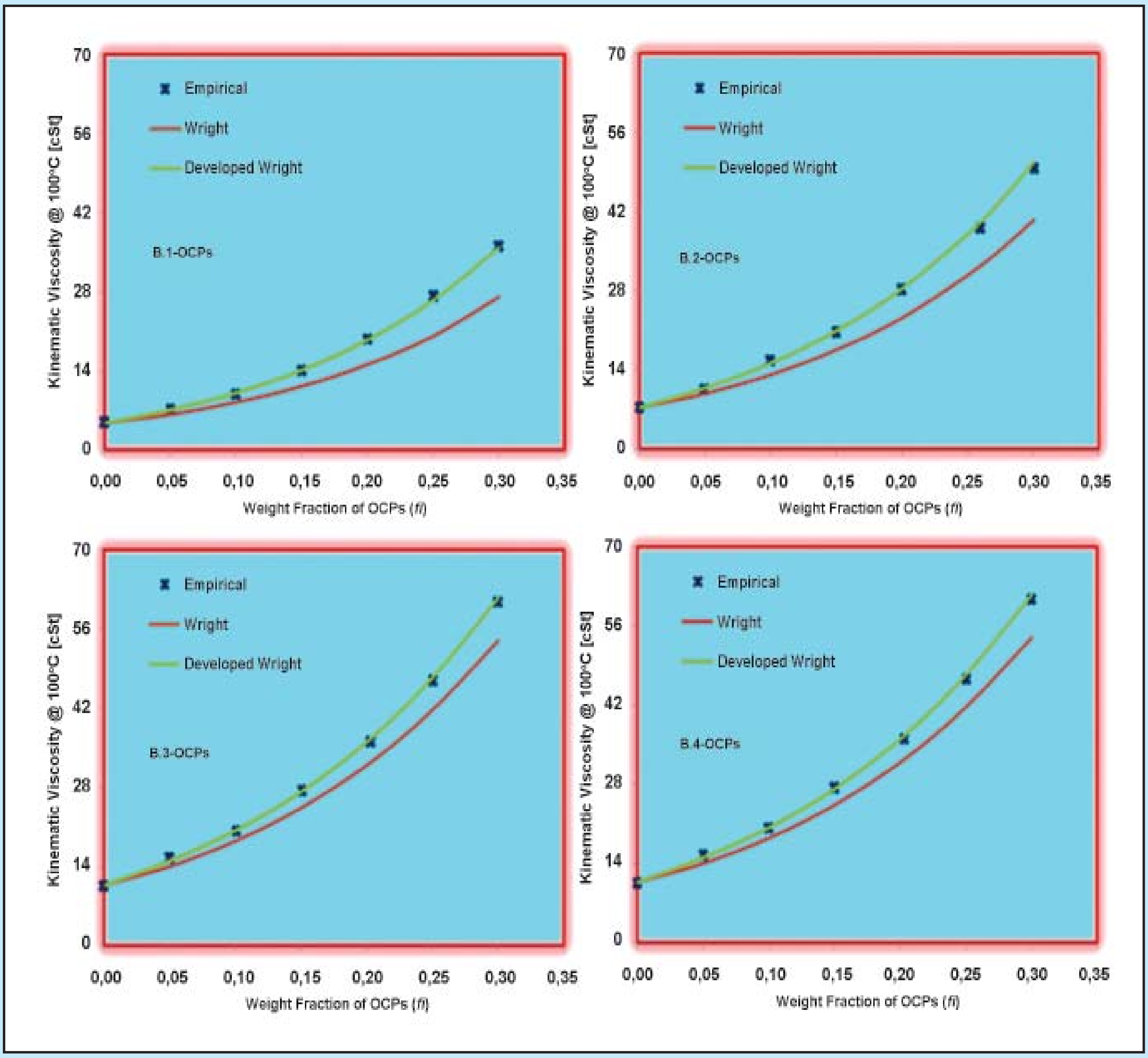

Figure 8
Kinematic viscosity of base oil-OCPs liquid-binary mixtures at 100°C
(*source: Author's data evaluation*)

with specific constant parameters as follow:

a_i [Base oil] = 1

$$\alpha_i\,[OCPs\,] = 9.05\ x\ 10^{-4}\ x\ \upsilon_{BO} + 0.848$$

$$\alpha_c = 1.26\ x\ 10^{-4}\ x\ \upsilon_{BO} + 0.987$$

Kinematic viscosity is calculated from dimensionless number (W_B) in Eq. 6 for Wright's method and Eq. 17 for Developed-Wright's method, proceeded with Eq. 7 to Eq. 9. The result shows that the new method has higher accuracy than the previous (Figure 7 and Figure 8). The addition of specific constants parameter (á) minimizes the deviations of estimated values. The average deviation of Developed-Wright's method at 40°C and 100°C becomes 2.056% and 1.917% respectively, lower than Wright's method which are 8.341% and 14.696%, meanwhile the maximum deviation reaches 5.821 % and 4.657%, lower than Wright's method, which are 21.256% and 25.265% respectively (Table 1). These values indicate that the proposed equation has better accuracy.

Table 1
Comparation of Wright's Method and Developed Wright's Method on Kinematic Viscosity Estimation

No	Base Oil Type	OCPs	% AD			
			Data measured at 40°C		Data measured at 100°C	
		[weight fraction]	Wright	Developed Wright	Wright	Developed Wright
1.	B.1	0.050	8.227	0.959	11.987	0.654
2.		0.100	13.515	0.161	14.579	2.492
3.		0.150	16.969	0.562	19.470	0.585
4.		0.200	19.071	0.816	22.905	1.002
5.		0.251	20.386	0.771	25.265	2.139
6.		0.300	21.256	0.608	25.184	0.708
7.	B.2	0.050	4.758	0.624	7.329	2.275
8.		0.100	7.046	1.409	15.362	1.876
9.		0.150	8.052	2.414	15.292	1.340
10.		0.200	9.288	2.530	17.595	0.702
11.		0.260	9.153	4.029	17.080	3.012
12.		0.301	10.122	3.690	18.314	2.236
13.	B.3	0.050	0.795	0.078	8.538	2.631
14.		0.100	1.043	0.341	8.577	0.317
15.		0.150	1.525	0.190	10.449	0.031
16.		0.203	1.341	0.593	10.104	1.553
17.		0.250	1.372	0.750	10.851	1.306
18.		0.300	1.199	1.195	11.232	1.230
19.	B.4	0.050	3.727	2.371	6.482	3.146
20.		0.104	5.710	4.142	11.010	3.466
21.		0.162	7.598	4.825	14.449	3.168
22.		0.200	8.544	5.055	16.057	2.906
23.		0.250	9.439	5.406	17.659	2.574
24.		0.300	10.052	5.821	16.925	4.657
Average Absolute Deviation [%AAD]			**8.341**	**2.056**	**14.696**	**1.917**
Maximum Deviation [% AD]			**21.256**	**5.821**	**25.265**	**4.657**

(*source: Author's data evaluation*)

V. CONCLUSION

Development of Wright's method to estimate kinematic viscosity of liquid-binary mixtures involving strong non-Newtonian fluids can be done by adding specific constants (α_i and α_c) to the equations. These specific constants indicate the interaction of fluid in the mixtures. The results show that the addition of those constants could minimize the deviations of estimated values. Development of Wright's method results in the specific constants for base oils, OCPs, and their combination respectively, α_i [Base oil] = 1; and $\alpha_c = 1.26 \times 10^{-4} \times \nu_{BO} + 0.987$. The average deviation on kinematic viscosity estimation at 40 °C and 100°C becomes 2.056 % and 1.917% respectively, lower than Wright's method which are 8.341% and 14.696%, while the maximum deviation reaches 5.821% and 4.657%, lower than Wright's method which are 21.256 % and 25.265% respectively (Table 1). These values indicate that the proposed equation has better accuracy.

REFERENCES

1. **Abu-Eishah,** 1999, A New Correlation for Prediction of the Kinematic Viscosity of Crude Oil Fractions as a Function of Temperature, API Gravity, and 50 % Boiling-Point Temperature, *International Journal of Thermophysics*, Vol. 20, No. 5, 1425-1434.
2. **Annual Book of ASTM Standard**, Vol. 05.04., 2009, ASTM D 7152-05^{e1} "*Standard Practice for Calculating Viscosity of a Blend Petroleum Product*", USA : ASTM International.
3. **Annual Book of ASTM Standard**, Vol. 05.01., 2009. ASTM D 445-06, *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)*. USA : ASTM International.
4. **Bair, S., *et al.*,** 2001, The temperature, pressure and time dependence of lubricant viscosity, *Tribology International* 34, 461–468.
5. **Booser, E.R.**, 1996, *Handbook of Lubricant Theory and Practice of Tribology*, (Vol.I), *Aplication and Maintenance*. Florida.
6. **Booser, E.R.**, 1996, *Handbook of Lubricant Theory and Practice of Tribology*, (Vol.II), *Aplication and Maintenance*. Florida.
7. **Diaz, R.M., *et al.***, 1996, Prediction of the viscosity of lubricating oil blends at any temperature, *Fuel,* Vol. 75, No. 5, 574-578.
8. **Fein, R.S.**, 1992, *Liquid Lubricants*, (ASTM Handbook Vol.18) *Friction, Lube and Wear Test*. USA : ASTM International.
9. **Freeman, P.**, 1962, *Lubricantion and Friction*, USA : Sir Isaac Pitman & Sons Ltd.
10. **Kurano, Y., *et al.***, 1992, "An Accurate Estimation Method of Kinematic Viscosity for Standard Viscosity Liquids", *International Journal of Thermophysics, Vol. 13, No. 4*.
11. **Maples, R.E.**, 2000, *Petroleum Refinery Process Economics*, (2nd Edition). Oklahoma : Pennwell Books, ISBN 0-87814-779-9.
12. **O'Connor and Boyd**., 1968, *Standard Handbook of Lubrication Engineering*, New York : McGraw Hill Inc.
13. **Rahmes, M.H.,** and **W.L. Nelson,** 1948, Viscosity Blending Relationship of Heavy Petroleum Oil, *Analytical Chemistry* Vol. 20, No. 10.
14. **Sovilj, M.,** 1995, Kinematic Viscosity-Composition Data For Ternary Liquid Systems, *Bulletin of the Chemists and Technologists of Macedonia*, Vol. 14, No. 2, 73 -78.
15. **Srinivasan, S., *et al***., 2007, *Viscosity Modifier for Lubricant Compositions*. USA : US Patents Publication.
16. **Valeri, D., and Meirelles,** 1997, Viscosities of Fatty Acids, Triglycerides, and Their Binary Mixtures, *JAOCS*, Vol. 74, no. 10. 1221-1226.
17. **Viswanath, D.S., *et al.*,** 2007, *Viscosity of Liquids : Theory, Estimation, Experiment, and Data*. Netherlands : Springer.
18. **Wartawan, A.L.**, 1998, *Pelumas Otomotif dan Industri*, Jakarta : Balai Pustaka.
19. **Wright, W.A.,** 1946. Prediction of Oil Viscosity Blending. *American Chemical Society, Atlantic City Meeting*. ˇ