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Estimating the Absorption of Volatile Organic Compounds in Four Biodiesels Using the UNIFAC Procedure

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Abstract**—**This work considered the thermodynamic feasibility of scrubbing volatile organic compounds into biodiesel in view of designing a gas treatment process with this absorbent. A detailed vapour – liquid equilibrium investigation was performed using the original UNIFAC group contribution method. The four biodiesels studied in this work are methyl oleate, methyl palmitate, methyl linolenate and ethyl stearate. The original UNIFAC procedure was used to estimate the infinite dilution activity coefficients of 13 selected volatile organic compounds in the biodiesels. The calculations were done at the VOC mole fraction of $9.213\text{x}10^{-8}$. Ethyl stearate gave the most favourable phase equilibrium. A close agreement was found between the infinite dilution activity coefficient of toluene found in this work and those reported in literature. Thermodynamic models can efficiently be used to calculate vast amount of phase equilibrium behaviour using limited number of experimental data.

Keywords**—**Biodiesel, Equilibrium, Gas treatment, Infinite dilution, Thermodynamic

I. INTRODUCTION

THE fatty acid methyl esthers (FAME) better known as biodiesel is a mixture with high boiling point, low toxicity, low volatility and high dissolving power in organic compounds. These characteristics make biodiesel a suitable solvent in absorption process such as the removal / recovery of volatile organic compounds from industrial waste gas streams. For efficient design of absorption equipment or any other separation processes which are diffusional in nature requires quantitative understanding of vapour liquid equilibrium (VLE). In order to use biodiesel effectively as an absorption solvent for a specific waste gas problem, it is important to determine the activity coefficients at infinite dilution of the VOCs under consideration in biodiesels. Scrubbing of the waste gases using selective high – boiling solvents is a reversible technique, which allows for both the cleaning of the waste gas and recovery of the VOC. In this study, infinite dilution activity coefficients of VOCs were estimated using the Original UNIFAC model (Fredenslund et al., 1975, 1977) [1], [2].

II. ABSORPTION THEORETICAL CONSIDERATIONS

The basic theory for the absorption and desorption cycles is based on Raoult’s law modified for non ideality (1).

$$p_i = \gamma_i x_i p_i^o \tag{1}$$

Where p_i is the equilibrium vapour pressure of component *i* at the system temperature; γ_i is the activity coefficient of component *i* in the absorbent, x_i is the mole fraction of component *i* in the liquid; and p_i^o is the vapour pressure of pure component at the system temperature. If the gas stream containing component *i* is contacted with an absorbing liquid, then the net flow of the component will always be from the gas into the liquid as long as its partial pressure is above the equilibrium vapour pressure of that component in the liquid. On the other hand it will be desorbed if the partial pressure is below the equilibrium level. From (1) it can be deduced that to get essentially complete absorption of any component from an air stream in the absorption tower, then the gas leaving the top of the tower must be in contact with an absorbing liquid essentially free of that component so that its equilibrium vapour pressure is zero. This means that unless chemical absorption is employed, there can be no recycle around the absorption tower itself. In any application, the first absorbent to be considered should be water. However, the use of water is limited in the scrubbing of VOCs as it quickly saturates.

III. GROUP CONTRIBUTION METHODS

The concept of group contribution method provides a correlation between limited experimental data with confidence of activity coefficients of those mixtures where there is little or no experimental data. With a group contribution method we have to know the functional groups which make the molecules. Each molecule is considered as the sum of the functional groups which constitute the molecule. Thermodynamic properties of a solution are then correlated in terms of the functional groups which comprise the mixture. A promising method for calculating activity coefficients from group contribution methods is the UNIFAC (Universal quasi chemical functional group activity coefficient model).

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A. The UNIQUAC Model

The UNIQUAC (Universal quasi chemical) is an activity coefficient model used to describe phase equilibrium [3] [Abrahams, Prausnitz 1975]. This is a lattice model and has been derived from first order approximations of interacting molecule surfaces in statistical thermodynamics. However, this model is not thermodynamically consistent due to its two liquid mixture approach. In this approach the local concentration around one central molecule is assumed to be independent from the local composition around another type of molecule. The UNIQUAC model also serves as the basis of the development of the UNIFAC group contribution method.

B. The UNIFAC model

The UNIFAC method is a semi-empirical system for the prediction of non-electrolyte activity estimation in non-ideal mixtures. UNIFAC uses the functional groups present on the molecules that make up the liquid mixture to calculate activity coefficients. By utilizing interactions for each of the functional groups present on the molecules, as well as some binary interaction coefficients, the activity of each of the solutions can be calculated. The principle, procedure, assumptions and the equations of the UNIFAC are well documented in literature including the works of [4] – [7].

IV. PROCEDURE

The calculations were performed using the Microsoft Excel program which offered highly acceptable simulation values

A. Combinatorial Part

- Obtain v , Q_i and R_i for each of the functional group
- Calculate r_i by using

$$r_i = \sum v_k^i R_k \tag{2}$$

- Then calculate q_i by using

$$q_i = \sum v_k^i Q_k \tag{3}$$

- Then calculate l_i by using

$$l_i = 5(r_i - q_i) - (r_i - 1) \tag{4}$$

- Then calculate ϕ_i by using

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \qquad (5)$$

(5)

- Then calculate θ_i by using

$$\theta_i = \frac{x_i k_i}{\sum_j x_j q_j} \tag{6}$$

- Therefore calculate $\ln\gamma_i^c$ by using

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} - \frac{z}{x_i} q \left(\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right) \tag{7}$$

B. Residual Part

- Obtain a_{mn} values
- From there calculate ψ_{mn} from

$$\psi_{mn} = \exp\left[\frac{-a_{mn}}{T}\right] \tag{8}$$

- Then calculate X_m by using

$$X_m = \frac{\sum_j v_m^i x_j}{\sum_{j,n} v_n^i x_j} \tag{9}$$

- Then calculate θ_m by using

$$\theta_m = \frac{Q_m x_m}{\sum_n Q_n x_n} \tag{10}$$

- Then calculate Γ_k and $\Gamma_k^{(i)}$ from

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{mk}}{\sum_n \theta_n \psi_{nm}} \right] \tag{11}$$

- Thereafter calculate $\ln\gamma_i^r$ from

$$\ln \gamma_i^r = \sum_k v_k^i (\ln \Gamma_k - \ln \Gamma_k^i) \tag{12}$$

- Then, $\ln\gamma_i^\infty = \ln\gamma_i^c + \ln\gamma_i^r$ (13)

V. RESULTS AND DISCUSSION

TABLE I
MOLE FRACTION BASED INFINITE DILUTION ACTIVITY COEFFICIENTS IN 4 BIODIESELS

	Biodiesels			
VOC	Methyl Palmitate	Methyl Oleate	Methyl Linolenate	Ethyl Stearate
Pentane	0.667	0.654	0.805	0.603
Hexane	0.739	0.766	0.747	0.686
Heptane	0.801	0.684	0.786	0.753
Triethylamine	0.785	0.8	0.795	0.729
Toluene	0.454	0.619	1.06	0.44
Xylene	0.715	0.463	0.887	0.718
Cyclohexane	0.671	0.66	0.613	0.616
Butylacetate	0.78	0.773	0.805	0.72
Diethylether	0.625	0.628	0.916	0.566
Chloroform	0.8	0.707	0.581	0.707
Acetone	1.798	1.959	2.235	1.595
Ethyl methyl ketone	1.521	1.782	1.833	1.365
Isobutyl methyl ketone	1.211	1.163	1.217	1.081

TABLE II
WEIGHT FRACTION BASED INFINITE DILUTION ACTIVITY COEFFICIENTS IN 4 BIODIESELS

	Biodiesels			
VOC	Methyl Palmitate	Methyl Oleate	Methyl Linolenate	Ethyl Stearate
Pentane	2.5	2.668	3.262	2.613
Hexane	2.318	2.635	2.534	2.487
Heptane	2.162	0.546	2.295	2.348
Triethylamine	2.098	2.343	2.297	2.253
Toluene	1.334	3.41	1.965	1.492
Xylene	1.821	2.478	1.275	2.113
Cyclohexane	2.155	2.325	2.129	2.289
Butylacetate	1.817	1.972	2.027	1.936
Diethylether	2.281	2.513	3.613	2.385
Chloroform	1.406	1.363	1.104	1.437
Acetone	8.371	9.998	11.256	8.583
Ethyl methyl ketone	5.705	7.327	7.433	5.915
Isobutyl methyl ketone	3.849	4.049	4.183	3.969

The mole and weight fraction based infinite dilution activity coefficients are shown in Tables 1 and 2. The values of the infinite dilution activity coefficients found in this work are generally very low well below 100. This is the opposite when compared to the most important industrial solvent water, which exhibits great non nonideality with organics. These results show that the four biodiesels can be used to scrub volatile organic compounds from contaminated industrial air effluents.

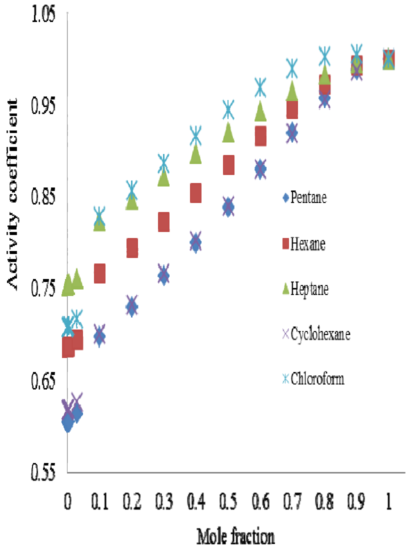

Fig. 1a Variation of activity coefficients with mole fraction in methyl palmitate

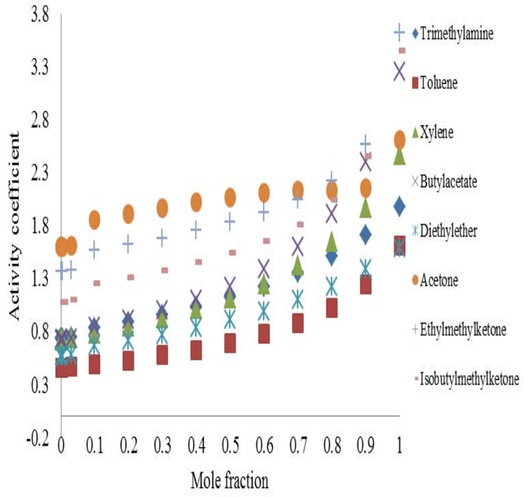

Fig. 1b Variation of activity coefficients with mole fraction in methyl palmitate

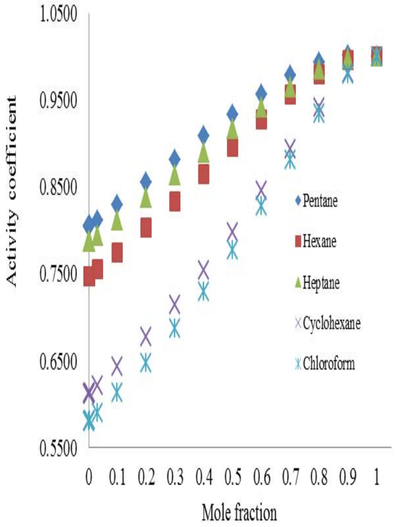

Fig. 2a Variation of activity coefficients with mole fraction in methyl linolenate

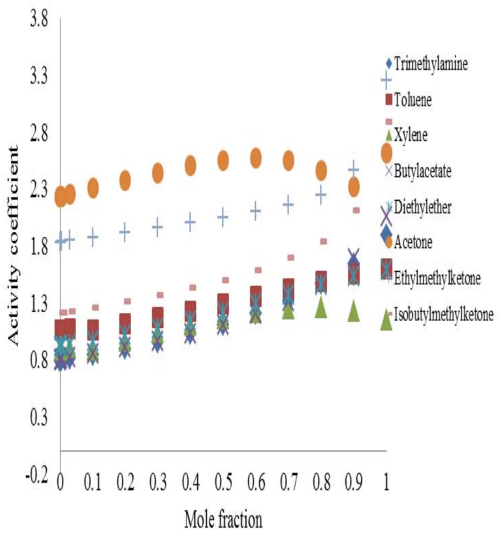

Fig. 2b Variation of activity coefficients with mole fraction in methyl linolenate

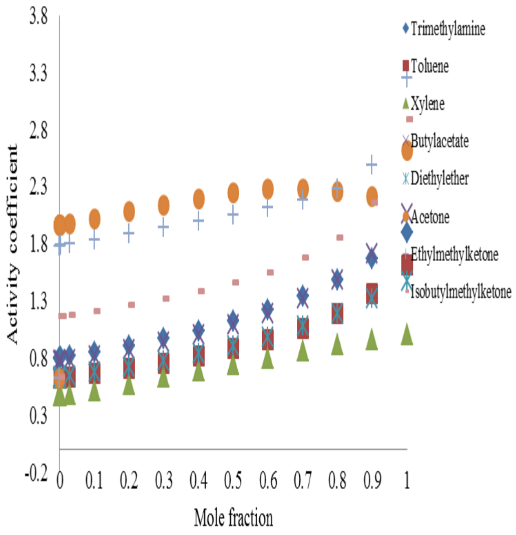

Fig. 3b Variation of activity coefficients with mole fraction in methyl oleate

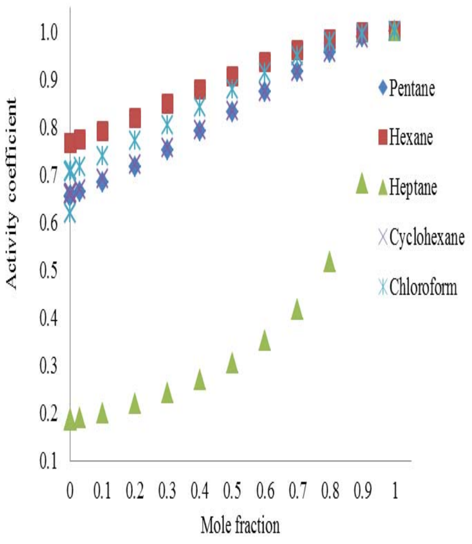

Fig. 3a Variation of activity coefficients with mole fraction in methyl oleate

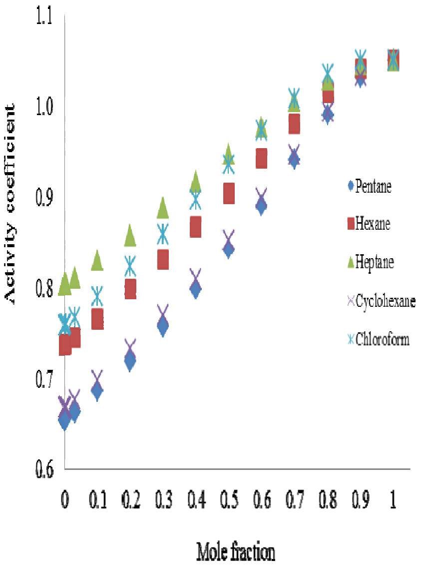

Fig. 4a Variation of activity coefficients with mole fraction in ethyl stearate

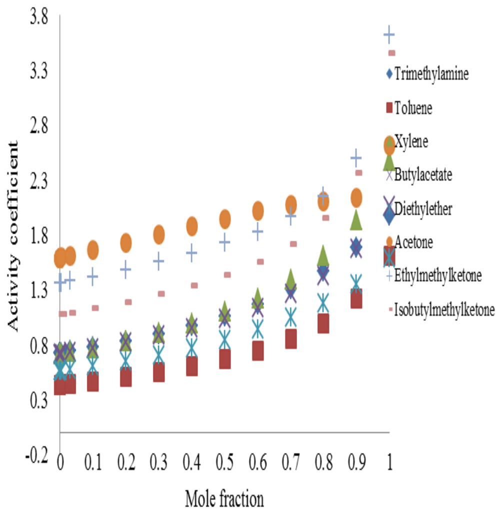

Fig. 4b Variation of activity coefficients with mole fraction in ethyl stearate

Figs 1a to 4b show the variation of activity coefficients with mole fraction. All the eight graphs show some high negative deviations especially figs1a, 2a, 3a and 4a. Figs 1a, 2a, 3a and 4b show a typical variation where activity coefficients increase with mole fraction approaching 1 as the mole fraction approaches 1.

The feasibility of a waste gas treatment using biodiesel can only be justified after careful economic considerations. In addition to the initial investment costs, the economic estimation will depend mostly on the operating costs which are mainly governed by the amount of solvent circulating in the process. The VLE data for different VOCs in waste gases can be used to determine the required amount of biodiesel for the absorption process. The UNIFAC procedure was used to estimate the VLE data for different organics in the four biodiesels.

V. CONCLUSION

This paper presents the vapour liquid equilibrium data for 13 volatile organic compounds in four biodiesels using the UNIFAC procedure. The UNIFAC procedure like other group contribution methods can reliably predict phase equilibrium data, and are time and cost saving. The required properties of the main component of biodiesel are widely available in most data bases. Biodiesel is a good absorption medium for volatile organic compounds considered in this work because of the very low activity coefficients, i.e. good solubility in the solvent.

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