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DETERMINATION OF HYDROXYL VALUE OF PALM-BASED POLYOLS BY PARTIAL LEAST SQUARES ALGORITHM USING NIR SPECTROSCOPY

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ABSTRACT

Near infra-red (NIR) spectroscopy with partial least square (PLS) regression of the results was developed as a rapid method for the determination of the hydroxyl value (HV) for palm-based polyols. The best NIR PLS calibration models to predict HV were developed in two types of spectral regions, Model 1 at 6500-8100 cm^{-1} *and Model 2 at 4500-10 005 cm*$^{-1}$*. For Model 1, the NIR-generated calibration plots had coefficients of determination (*R^2*) of 0.991 and a standard error of calibration (SEC) of 3.23, while the validation plots had* R^2 *of 0.994 and a standard error of prediction (SEP) of 2.96. For Model 2, the calibration plot had* R^2 *of 0.997 and SEC of 2.32, while the validation plots had* R^2 *of 0.998 with SEP of 2.52.*

Keywords: palm-based polyols, hydroxyl value, near infra-red spectroscopy, partial least square regression.

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INTRODUCTION

A polyol is a polymeric alcohol having at least two reactive hydroxyl groups in the molecule. About 90% of the polyols used worldwide in polyurethane foam (PUF) production are petroleum-based. The polyurethane industry covers a wide range of applications. It is known that petrochemical resources are limited and may be depleted over time. Thus, the chemical industry is actively looking at vegetable oils as a green alternative source for polyol production as they are unlimited, renewable, cheap and more biodegradable. Moreover, bio-based polyols can produce PUF free of volatile organic compounds (VOC). Some examples are polyurethane coatings and floorings, adhesives and thermoplastic polyurethanes.

Natural oils such as castor oil have the hydroxyl functionality that can be used directly for PUF production. However, vegetable oils like soyabean oil, linseed oil, rapeseed oil and palm oil need to be altered chemically in order to introduce the hydroxyl groups into the unsaturated bonds in their triglyceride structures. This can normally be achieved through epoxidation of the double bonds followed by ring opening with alcohols, amino alcohols or acids. The Malaysian Palm Oil Board through its Advanced Oleochemical Technology Division (AOTD) is working closely with local industry to develop and commercialise palm-based polyols.

The hydroxyl value (HV) is expressed as milligrams (mg) of potassium hydroxide (KOH) per gram of oil. HV of a polyol is an important parameter in formulating polyurethane products. It can be used to determine the extent of reaction or number of hydroxyl groups available for reaction with isocyanates, another major ingredient in PUF production. Polyol manufacturers use HV as part of the process control and quality assurance programme for the production of polymers.

The titration method commonly used for HV analyses is according to the American Oil Chemists' Society publication on HV determination (AOCS Cd 13-60). The accuracy of this method can be

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quite dependant on the skill of the analyst, and on the chemicals used, especially acetic anhydride. Acetic anhydride is not easily obtained as it is a controlled chemical in Malaysia, registered under the Malaysian Ministry of Health. Disadvantages of the method are that it is time-consuming, labour-intensive and involves the use of large amounts of hazardous reagents, *e.g.* pyridine and acetic anhydride.

Spectroscopic methods such as near infra-red (NIR) and Fourier transform infra-red (FTIR) are possible candidates to overcome most problems associated with chemical analyses for HV. Lee *et al*. (1990) reported the use of FTIR for the determination of the hydroxyl number of petroleum-based polyester samples. Godoy *et al*. (2007) reported the use of FTIR spectroscopy equipped with horizontal attenuated total reflectance (HATR) for HV analyses in polyols. Kemper *et al*. (2001) reported the use of the Fourier transform near-infrared (FT-NIR) spectroscopy for the determination of HV, acid number and other critical polyol properties.

In this present work, an NIR spectroscopy method using a partial least square (PLS) algorithm was developed for the prediction of HV for palm-based polyols synthesised by the Polymer and Composite Group in AOTD.

MATERIALS AND METHODS

Determination of Acid Number and Hydroxyl Value by Chemical Methods

The acid number (AN) and HV of the calibration standards and validation samples (palm-based polyols) were determined by AOCS Standard Methods (Cd 3a -63 and Cd 13-60, respectively).

General Polyol Sample Treatment

The various palm-based polyol samples used as the calibration standards were first homogenised in an oven at about 50°C for 20 min for samples with lower viscosity (<1000 mPa.s at 25°C) and at 65°C for 60 min for those which were more viscous (>1000 mPa.s at 25°C) prior to NIR analysis.

Calibration Standards

Palm-based polyols were used as calibration standards and for the validation of the calibration models. Palm olein (POo)-based polyol (POP pioneer and Poly-EG); palm kernel oil (PKO)-based polyol; blends of different ratios of POo with PKO-based polyol (POP primer), blends of a certain ratio of PKO with another highly unsaturated vegetable oil-based polyol (POP premier) and palm oleic acid-based polyol (PolyMO) were all synthesised by the Polymer and Composite Group in AOTD. These represent examples of polyols from different starting materials and having different hydroxyl values.

The AN and HV of the calibration standards and validation samples (palm-based polyols) were determined by AOCS Standard Methods (Cd 3a -63 and Cd 13-60, respectively).

Instrumentation

The instrument used for NIR absorbance and spectra records was an ABB Bomem (Canada) MB series FT-NIR spectrophotometer with AIRS (Advance IR Software) software and equipped with standard chemometric packages.

The calibration standards comprising palm-based polyols were transferred into standard 7 mm diameter disposable vials for measurements. The vials were then placed directly in the transmission sampling compartment. Four spectra were collected for each calibration standard and for each of the various samples. In these studies, spectra were collected from 8100-6500 cm^{-1} for Model 1 and from 4500-10 005 cm^{-1} for Model 2 using Galactic Industries PLS Plus, PLS Plus/IQ and Infometrix Piroute chemometric software. PLS algorithms were used to derive the quantification models.

Calibration Models

The numerical relationships between the HV obtained from the NIR spectrum and that from the standard chemical method were determined using the AIRS software. The software provides a PLS regression statistical approach for the mathematical treatment of the NIR predicted data. A PLS calibration plot was generated. The accuracy of the PLS model was based on both the smallest root mean square error of calibration (SEC) and the highest coefficient of determination (R^2).

Validation

The 'leave-one-out' cross-validation test was used to test the calibration models using the set of standards, 43 (Model 1) and 39 (Model 2) used in the calibration models. The software removes one sample from the calibration set and performs an entire PLS calibration with the remaining samples, then makes a prediction for the sample left out during calibration. The procedure continues iteratively until each of the samples has been left out once. The predicted HV for each of the samples was then compared to the known HV of this reference sample. The calibration factors were optimized, guided by the predicted residual error sum of squares (PRESS) test when the minimal factors were obtained. PRESS values are indicators of how closely a model fits the calibration data. The accuracy of the models was assessed by the standard error of cross-validation (SECV) and R^2.

For further evaluation of the calibration models, another set of palm-based polyols spectra were used for external validation of the PLS calibration models. The standard error of prediction (SEP) and R^2 from the validation plot were used to assess the accuracy of the models.

RESULTS AND DISCUSSIONS

Palm-based polyols with different hydroxyl functionality synthesised in AOTD were used as the calibration set. The method of synthesis for the various palm-based polyols was by epoxidation of palm oil followed by reaction with polyhydric alcohols under catalytic conditions (Hassan *et al.*, 1993; Tuan Noor Maznee *et al.*, 2008). The PolyMO polyol was prepared using oleic acid and glycerol (Hoong *et al.*, 2008). The use of synthesised soyabean oil-based polyols with different hydroxyl functionality as the calibration standards for determination of HV of soyabean-based polyols by FTIR has also been reported (Godoy *et al.*, 2007).

Figure 1 shows an overlay of the NIR spectra that were considered representative of all the different palm-based polyol samples used as calibration standards. From a comparison of the spectra, it is obvious that the hydroxyl combination band of the various types of palm-based polyols varied with OH concentration.

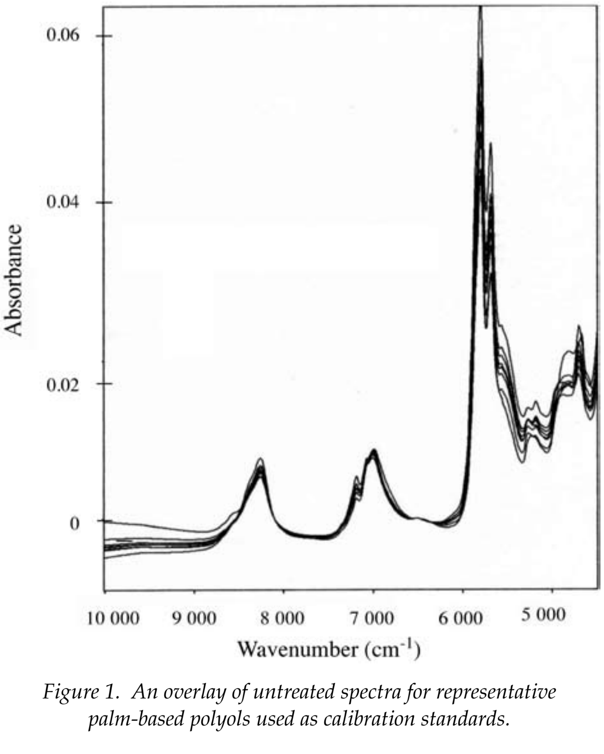

Figure 1. An overlay of untreated spectra for representative palm-based polyols used as calibration standards.

Two calibration models with good linear relationships were derived based on the sub-region of 6500-8100 cm^{-1} (Model 1), inclusive of the first hydroxyl overtone region (Kemper *et al.*, 2001) and the NIR whole spectrum between 4000-10 005 cm^{-1} (Model 2). The two models were compared to find the more optimum model. The quality of the models was evaluated based on the SEC, SEP and SECV.

Model 1 Covering Sub-region 6500-8100 cm^{-1}

Forty-three palm-based polyol samples with HV ranging from 55 to 250 mg KOH g^{-1} of sample were used as calibration standards. A PLS calibration model was built and optimised in the region of 6500-8100 cm^{-1}. PLS was chosen because of its ability to perform measurements even if there were severe spectral overlaps, component matrix interactions, or underlying absorptions which would affect the spectra as the concentration of all components changed. *Figure 2* shows a high R^2 of 0.991 at 99% confidence obtained for Model 1. The SEC was 3.23. *Figure 3* shows the plot of the SECV *vs.* the different

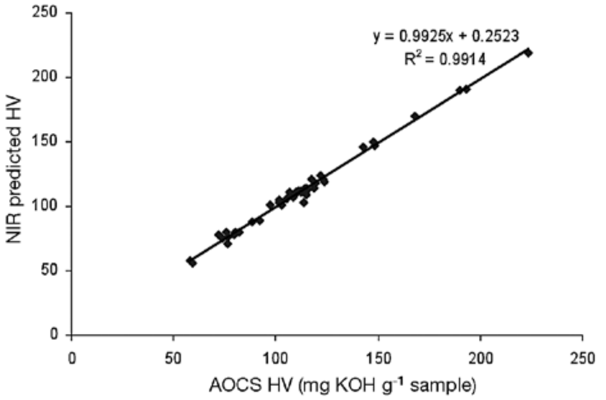

Figure 2. Plot of hydroxyl values (HV) of palm-based polyols by American Oil Chemists' Society (AOCS) chemical method vs. *near infra-red (NIR) partial least square predicted hydroxyl value (HV) for calibration.*

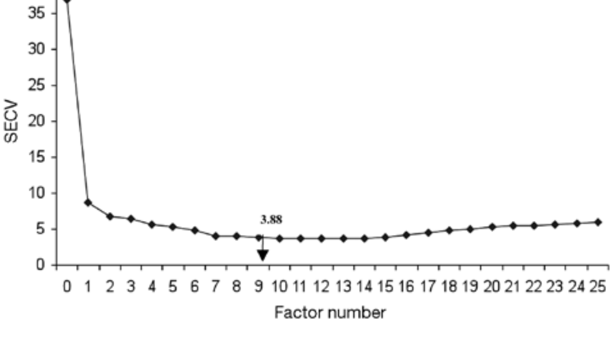

Figure 3. Plot of standard error of cross validation (SECV) vs. *the different number of factors included in the cross validation of the partial least squares (PLS) model for hydroxyl value in palm-based polyol.*

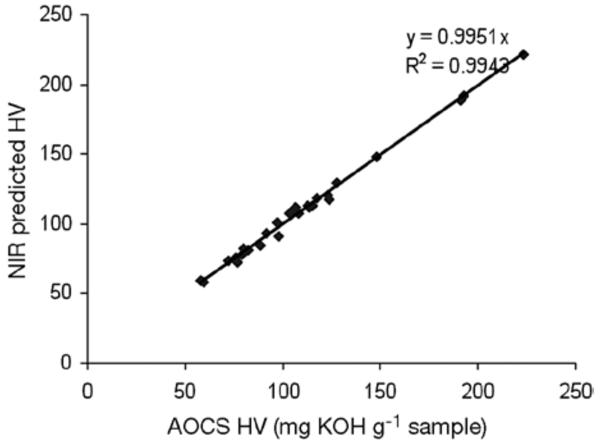

Figure 4. Plot of hydroxyl values (HV) of palm-based polyols by American Oil Chemists' Society (AOCS) chemical method vs. *near infra-red (NIR) partial least square predicted HV for validation.*

number of factors included in the cross-validation of PLS of Model 1. The number of factors of 9 was optimum as it resulted in the minimum SECV of 3.88. This SECV value was close to the value of SEC which then shows that the calibration carried out was feasible.

Twenty-eight palm-based polyols of the same formulation variety as the calibration standards were used as the bases for validating the calibration model. *Figure 4* shows the validation plot resulting in R^2 of 0.994. A partial listing of the predicted OHV values is shown in *Table 1*. The results show that the majority of NIR-predicted OHV had less than 6% difference from the values determined by the AOCS titration method.

TABLE 1. PARTIAL LISTING OF EXTERNAL VALIDATION DATA AMERICAN OIL CHEMISTS' SOCIETY (AOCS) HYDROXYL VALUES AND NEAR INFRA-RED (NIR) PREDICTED HYDROXYL FOR PALM-BASED POLYOL

AOCS hydroxyl values (mg KOH g^{-1} of sample)[a]	NIR predicted hydroxyl values ± SD (RSD)[b]	% different to AOCS method
75.9	76.3 ± 1.8 (2.4)	0.5
82.4	80.6 ± 0.7 (0.9)	2.2
79.8	78.4 ± 0.6 (0.8)	1.8
58.3	59.5 ± 2.2 (3.7)	2.0
78.9	78.2 ±. 0.5 (0.6)	0.9
59.6	57.8 ± 0.5 (0.9)	3.1
97.3	101.0 ± 0.5 (0.5)	3.8
111.0	110.7 ± 0.1 (0.1)	0.3
88.7	84.1 ± 0.3 (0.4)	5.2
92.1	93.5 ± 0.3 (0.3)	1.5
142.8	148.6 ± 1.4 (0.9)	4.1
114.0	115.6 ± 0.7 (0.6)	1.4
190.9	188.9 ± 1.3 (0.7)	1.0
192.9	191.8 ± 0.9 (0.5)	0.6
223.4	221.2 ± 7.2 (3.3)	1.0

Note: [a]mean of four analyses, [b]mean of four replicates.

Calibration Model 2 Covering Region 4500-10 005 cm^{-1}

Calibration Model 2 was derived using 39 palm-based polyol calibration standards, with HV between 58 and 230 mg KOH g^{-1} sample. The calibration model was developed covering the full NIR reflectance spectral range of 4500 cm^{-1} to 10 005 cm^{-1}. The rationale behind this was to find if there was any improvement in the predictive capability when a wider region was used. The whole spectrum method allowed the use of every single wavelength in a recorded spectrum, and therefore more spectral information would be factored into the optimisation of the calibration models, which may result in more robust calibrations. The resulting R^2 was 0.997 at 99% confidence. *Figure 5* shows the calibration plot of Model 2.

When the 'leave-one-out' cross-validation technique was carried out, and the plot of SECV *vs.* number of factors included in the cross-validation for Model 2 (*Figure 6*) was obtained, the number of factors of 14 was the optimum as it resulted in SECV values of 3.29. An external validation set of samples comprising palm-based polyols of similar variety as those of the calibration standards was used to validate Model 2. *Figure 7* shows the validation plot with R^2 of 0.998. The data from the prediction set are given in *Table 2*. NIR values were in good agreement with analytical laboratory values, and the difference was less than 6%.

Statistical Parameters

Table 3 shows the statistical data of the two calibration models (Model 1 and Model 2). It was found that very good R^2 values were obtained for both models. To further evaluate the quality of the models, the ratios of SEC/SEP were considered. It was observed that both models showed very good SEC/SEP ratios (close to unity) (Godoy

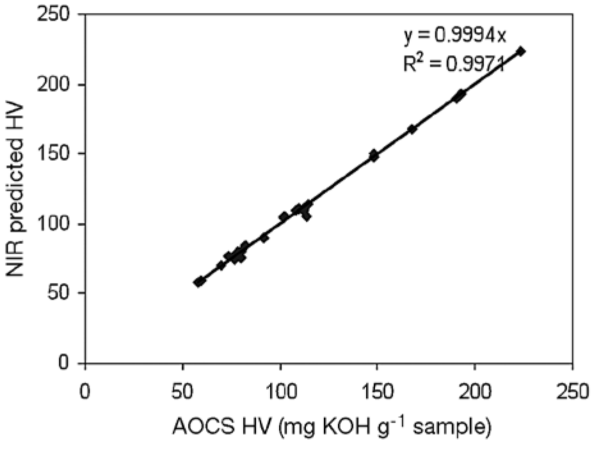

Figure 5. Plot of hydroxyl values (HV) of palm-based polyols by AOCS chemical method vs. *near infra-red (NIR) partial least square predicted HV for calibration.*

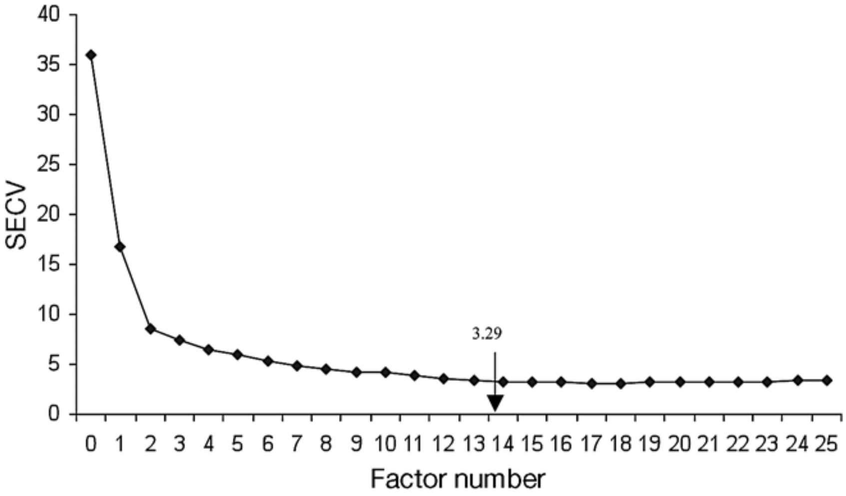

Figure 6. Plot of standard error of cross validation (SECV) vs. *the different number of factors included in the cross validation of the partial least squares model for hydroxyl value in palm-based polyol.*

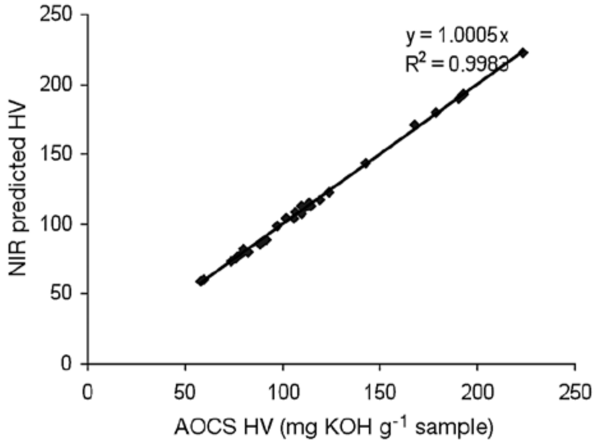

Figure 7. Plot of hydroxyl values (HV) of palm-based polyols by American Oil Chemists' Society (AOCS) chemical method vs. *near infra-red (NIR) partial least square predicted HV for validation.*

TABLE 2. PARTIAL LISTING OF VALIDATION SET DATA. HYDROXYL VALUES BY AMERICAN OIL CHEMISTS' SOCIETY (AOCS) AND NEAR INFRA-RED (NIR)

AOCS hydroxyl values (mg KOH g^{-1} sample)[a]	NIR predicted hydroxyl values ± SD (RSD)[b]	% different to AOCS method
76.0	75.7 ± 2.1 (2.8)	0.4
79.9	80.2± 3.3 (4.1)	0.4
76.5	76.5 ± 3.7 (4.8)	0.1
142.8	143.7 ± 5.1 (3.5)	0.7
88.7	86.0 ± 5.6 (6.5)	3.0
97.3	98.7 ± 5.6 (5.7)	1.4
117.0	117.1 ± 2.8 (2.4)	1.6
59.6	60.6 ± 5.3 (8.7)	1.8
190.2	191.8 ± 1.4 (0.7)	0.9
92.1	88.2 ± 0.4 (0.5)	3.5
109.9	107.2 ± 1.4 (1.3)	2.4
192.9	192.8 ± 1.5 (0.8)	0.1
123.9	122.9 ± 3.4 (2.8)	0.8
178.5	179.4 ± 0.9 (0.5)	0.5
58.3	59.6 ± 1.7 (2.9)	2.2
223.4	222.8 ± 1.6 (0.7)	0.3
167.7	170.6 ± 3.7 (2.2)	1.7
73.7	73.8 ± 0.5 (0.7)	0.1

Note: [a]mean of four replicates, [b]mean of four replicates.

et al., 2007). Overall, we see that the residual errors for calibration, cross-validation and prediction for Model 2 were lower than for Model 1. This means that Model 2 had a better predictive ability than Model 1. The use of the whole spectrum region slightly increased the performance of the calibration models. Comparison of the mean differences of the predicted values to the AOCS hydroxyl values showed the percentage mean differences were small, *i.e.* less than 3.5% for both models.

CONCLUSION

NIR together with a PLS algorithm proved to be very good for the determination of HV of palm-based polyols. Two types of models were built, based first on the region of 6500-8100 cm^{-1} (Model 1) and then on the entire region, 4500-10 005 cm^{-1} (Model 2). Model 2 showed slightly better performance based on the values of the correlation coefficient values (R^2, SEC, SECV and SEP). The NIR method as compared to the conventional chemical analyses had the advantages of being much faster (less than 2-3 min per sample); environmental-friendly (no solvent usage); traceable and suitable for a quality control site. The types of palm-based polyol samples that can be analysed must have a similar spectrum as those from the calibration sets. However, the method can be modified for other newly developed

TABLE 3. STATISTICAL PARAMETERS FOR NEAR INFRA-RED (NIR) PARTIAL LEAST SQUARES REGRESSION CALIBRATION MODELS IN THE SELECTED SPECTRAL REGION FOR QUANTIFICATION OF HYDROXYL VALUES IN PALM-BASED POLYOLS

Model	**1**	**2**
Region (cm^{-1})	**6 500 – 8 100**	**4 500 – 10 005**
SEC	3.23	2.32
SECV	3.88	3.29
SEP	2.96	2.52
SEC/SEP	1.09	0.92
R^2	0.991	0.997
Factors	9	14
MD to AOCS (%)	2.44± 2.05	1.44 ± 1.04

Note: MD – mean differences to American Oil Chemists' Society (AOCS) method.

palm-based polyol formulations by including them in the calibration sets and establishing a new model. This NIR method is a secondary method which provides a good approximation of HV. However, the accuracy of the method is very much dependent on the laboratory-obtained HV of the calibration standards.

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REFERENCES

ASSOCIATION OF OFFICIAL ANALYTICAL CHEMIST (2004). Hydroxyl value Cd 13-60. *Official Methods and Recommended Practices of the AOCS*. 5th ed. AOCS, Urbana, IL, USA.

GODOY, S C; FERRAO, M F and GERBASE, A E (2007). Determination of the hydroxyl value of soybean polyol by Attenuated Total Reflectance/ Fourier Transform Infrared Spectroscopy. *J. Amer. Oil Chem. Soc., 84*: 503-508.

HASSAN, H A; YEONG, S K and AHMAD, S (1993). Palm-based polyols for polyurethane foams. *Proc. of the 1993 PORIM International Palm Oil Conference - Chemistry and Technology Conference*. p. 227-235.

HOONG, S S; MOHD NORHISHAM, S; TUAN NOOR MAZNEE, T I; NURUL'AIN , H; HAZIMAH, A H; OOI, T L and SALMIAH, A (2008). Preparation of a low viscosity and light coloured fatty acid based polyol. *J. Oil Palm Research Special Issue*: 44-55.

KEMPER, M S; MCCARTHY, W J; NUNN, N S; LOWRY, S R and KEMENY, G J (2001). The use of Fourier Transform Near-infrared Spectroscopy to measure hydroxyl value, acid number and other parameters important to polyol production. Thermo Nicolet Corporation Technical Report at www.thermoNicolet.com

LEE, K A B; HURLEY, S M; SIEPLER, R A; MILLS, R D; HANDRICH, K A and CONWAY, J J (1990). Determination of hydroxyl number in polymers by infrared spectroscopy. *Applied Spectroscopy, 44(10)*: 1719 -1721.

TUAN NOOR MAZNEE, T I; NURUL'AIN, H; KOSHEELA DEVI, P P; MOHD NORHISHAM, S; HOONG, S S; YEONG, S K and HAZIMAH, A H (2008). Improved palm-based polyols: POP pioneer, POP primer and premier. *MPOB Information Series No. 394.*