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BIO-BASED CONTENT OF OLIGOMERS DERIVED FROM PALM OIL: SAMPLE COMBUSTION AND LIQUID SCINTILLATION COUNTING TECHNIQUE

(Kandungan Berasaskan Bio dalam Oligomer daripada Minyak Sawit: Teknik Pembakaran Sampel dan Penghitungan Sintilasi Cecair)

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Abstract

The bio-based content is defined as the ratio of weight of the bio-based carbon to the total organic carbon in the product. A radiocarbon technique, involving combustion of samples and counting of the resulting ^{14}C isotope, was applied to quantify the bio-based content of polyols derived from palm oil. The samples were combusted using a sample oxidizer and the carbon dioxide was trapped by a vapor-phase reaction with an amine, forming carbamate, which was then mixed with an appropriate scintillation cocktail. For the liquid scintillation counting, validation of the method was evaluated through recovery, while the quenching effect was corrected by constructing a quench curve. The optimized radiocarbon method was then applied to determine the ^{14}C activity (counts per minute [CPM] and disintegrations per minute [DPM]) of palm olein and the polyols derived from it. Palm olein were confirmed to have 100% bio-based content while the value for the polyols derived from them ranged from 71 to 96%, depending on the reactants used for ring-opening reaction of the epoxidized palm olein.

Keywords: palm olein polyol, renewable, radiocarbon, carbon dioxide trapping, quench

Abstract

Kandungan berasaskan bio ditakrifkan sebagai nisbah berat karbon berasaskan bio dengan jumlah karbon organik di dalam sesuatu produk. Teknik radiokarbon, yang melibatkan pembakaran sampel dan penghitungan isotop ^{14}C yang dihasilkan, telah digunakan untuk mengukur kandungan berasaskan bio dalam poliol daripada minyak sawit. Sampel dibakar menggunakan pengoksidasi sampel dan karbon dioksida diperangkap dengan amina, membentuk karbamat, yang kemudian dicampurkan dengan koktel sintilasi yang sesuai. Bagi penghitungan sintilasi cecair, ketepatan kaedah dinilai melalui pemulihan, sementara kesan pelindapkejutan dibetulkan dengan membina keluk pelindapkejutan. Kaedah radiokarbon yang dioptimumkan kemudiannya digunakan untuk menentukan aktiviti ^{14}C (hitungan per minit [CPM] dan disintegrasi per minit [DPM]) olein sawit dan poliol yang berasal daripadanya. Olein sawit disahkan mempunyai 100% kandungan berasaskan bio manakala poliol sawit berkisar antara 71 hingga 96%, bergantung kepada reaktan yang digunakan untuk tindak balas ke atas olein sawit yang teroksida.

Kata kunci: poliol olein sawit, boleh diperbaharui, radiokarbon, perangkap karbon dioksida, pelindapkejutan

Introduction

Polyurethane (PU) is extensively used in foams, composites, coatings, adhesives, sealants, and elastomers industry [1]. PU is produced by reacting polyols with isocyanates. Most of the polyols used in PU industry originate from petroleum-based source. Depleting resources of fossil energies and initiatives to reduce the emission of greenhouse gases have led to the development and use of renewable biomass resources [2]. Currently, these renewable resources, *e.g.* castor, soybean, canola and palm oils, have been successfully utilized as raw materials for polyols production [3-8]. These bio-based polyols have been subsequently incorporated in meaningful volumes in PU foam formulations [9-12].

In some countries, the bio-based content of biomass-based products need to be certified. ‘‘Biomass plastics mark’’ was authorized by Japan Bio-Plastics Association to certify biomass plastics in Japan which were made with at least 25% by weight of biomass to the total amount of the product. Certified products were then listed in the association’s positive list. Furthermore, ‘‘Biomass mark’’ was authorized by Japan Organics Recycling Association to certify biomass-based raw materials [13]. Meanwhile, the United States Department of Agriculture obliges companies in the United States that wished to join their ‘‘Bio-Preferred Voluntary Labelling Program’’ to submit the American Society of Testing and Materials (ASTM) D6866 product certification. Other certification bodies requiring ASTM D6866 bio-based content testing include Canada’s “EcoLogo” for the CCD-170 standard and Belgium’s “Vinçotte” for its OK Bio-based eco-label system.

The bio-based content is defined as the ratio of weight of the bio-based carbon in material to the total organic carbon in the product. The ASTM D6866 standard test method regulates that the bio-based content should be calculated from the percent of modern carbon. This standard regulates three measuring methods using ^{14}C concentration, *i.e.* by a liquid scintillation counter (LSC), accelerator mass spectrometry (AMS), or isotope ratio mass spectrometry.

All three methods were evaluated and it was found that the most accurate method was AMS and that the benzene synthesis and carbon absorption methods had lower accuracy [14]. The accuracy of all analysing methods, however, was acceptable. Culp et al. compared the accuracy and precision of ^{14}C between natural products and bio-based materials analysed by AMS and LSC. The results showed that accurate and precise ^{14}C measurements were achievable by both methods [15-18]. Each of the three methods has its own advantages and disadvantages. When comparing the duration and cost of analysis, the carbon absorption method is the most preferred method in the industrial application. These different methods have been used to verify bio-based additions to petrochemicals [19-22].

The method using radiocarbon technique requires the collection of carbon dioxide (CO_2) of a sample in a suitable absorbing solution. This was carried out using a sample oxidizer, in which the sample material was combusted in an oxygen-enriched atmosphere yielding water vapour and CO_2. Physical separation of ^{3}H and ^{14}C radionuclides was then achieved. The separated ^{14}C radionuclide was counted using an LSC. The counts were compared either directly or through secondary standards to the ^{14}C oxalic acid SRM 4990C with stated uncertainties. Significantly lower ^{14}C counts indicate the presence of ^{14}C-depleted carbon. Zero percent ^{14}C, when compared to the standard, signifies an entire lack of ^{14}C atoms in a material, thus indicating a petroleum-based carbon source.

The analysing method in this present study was performed using carbon absorption because of the simplicity of the process and the variation was acceptable. A radiocarbon technique, involving combustion of samples and counting of the resulting ^{14}C isotope, was applied to determine the bio-based content of vegetable oils as well as polyols derived from palm oil, fatty acid methyl ester and castor oil. After collecting CO_2 in a suitable absorbing solution, the CO_2 cocktails were submitted LSC analysis.

Materials and Methods

Chemicals and standards

Vegetable oils *i.e.* palm oil, canola oil, soybean oil, olive oil and sunflower oil were purchased from overseas supplier. Castor oil and its polyols (HCO-25, CO-25 and CO-5) were purchased from Troy Polymers Inc. USA.

Refined, bleached and deodorised palm olein was acquired from Southern Edible Oil Industries, Malaysia. Epoxidized palm olein (EPOo) and all the polyols resulting from the ring-opening with different alcohols were obtained from the Polymer and Composite group of Malaysian Palm Oil Board (MPOB) [7]. The ring-opening syntheses were conducted with different types of alcohol, *i.e.* methanol, 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, bio-based 1,3-propanediol, 1,5-pentanediol and 1,6-hexanediol; and the polyols obtained were denoted as POoP M, POoP E135, POoP PG, POoP PDO, POoP Bio PDO, POoP PTDO and POoP HDO, respectively. A commercial polyol was obtained from a local polyol producer.

Fatty acid methyl ester (FAME), containing 74.2% of $C_{18:1}$ methyl, was acquired from Carotino, Malaysia. Epoxidized FAME (E-FAME) and all the polyols resulting from the ring-opening with different alcohols were obtained from the Polymer and Composite group of MPOB [5]. The ring-opening syntheses were conducted with different types of alcohol, *i.e.* 1,3-propanediol, bio-based 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol and water; and the polyols obtained were denoted as PolyFAME PDO, PolyFAME Bio PDO, PolyFAME BDO, PolyFAME PTDO, PolyFAME HDO and PolyFAME H, respectively. Susterra® propanediol (DuPont, US) was used without further modification.

Amine (CarboSorb E) and scintillation cocktail (PermaFluor E+) were purchased from PerkinElmer (US). High DPM ^{14}C Spec Chec standard solution was purchased from PerkinElmer (US) with a radioactivity level of 826,000 DPM mL-1 ± 2.474 %. National Institute of Standards and Technology (NIST) standard reference material 4990C (oxalic acid) was purchased from PerkinElmer (US) with a ratio of ^{14}C massique activity of 1.2933 ± 0.0004.

Preparation of samples

All samples were homogenized before weighing. The liquid samples were weighed onto a combusto-pad, which were then placed on a combusto-cone.

Combustion of samples

Samples combustion was performed using a PerkinElmer Sample Oxidizer Model 307 (US). A portion of the sample was combusted until the absence of visible residue, which took 0.5 to 2 minutes. After the combustion, two separate samples; a sample of ^{3}H (water) and a sample of ^{14}C (CO_2) were trapped at ambient temperature in a 20 mL Teflon-coated low diffusion polyethylene vials (PerkinElmer).

The water was condensed in a cooled coil and was then washed into a vial where it was mixed with an appropriate scintillation cocktail (Monophase S). The CO_2 was trapped by a vapour-phase reaction with an amine (CarboSorb E), that formed into carbamate, which was then mixed with an appropriate scintillation cocktail (PermaFluor E+). The flow diagram of the 307 Sample Oxidizer is presented in Figure 1.

Counting of samples

After combustion, activity concentrations of ^{14}C isotopes of the samples were determined using a PerkinElmer Tri-Carb 2910TR Low Activity Liquid Scintillation Counter (Illinois, US) with an external standard (^{133}Ba) which allows the measuring of external spectral quench parameter (transformed spectral index of external standard [tSIE]). The analytical results were determined using QuantaSmart™ program.

A quench curve was constructed to determine the counting efficiency of each unknown sample. A quench standard curve is a series of standards in which the absolute radioactivity (DPM) per vial is constant and the amount of quench increases from vial to vial. A quench curve uses the relationship between counting efficiency and tSIE to correct the measured CPM to DPM. When a quench curve is made, the DPM value in each standard is known. Each standard was counted and the CPM was measured. The counting efficiency was calculated using Equation 1. At the same time, tSIE was measured for each standard. A correlation was made using the tSIE on

the X-axis and the counting efficiency on the Y-axis. A curve was fitted to the standard points.

The efficiency for each unknown sample was determined from the constructed quench curve using the measured tSIE value for each sample (Figure 2). At the same time, the CPM of the unknown sample was measured. Knowing the CPM of the unknown sample and the counting efficiency, DPM of the sample was then calculated according to Equation 2.

The DPM was compared directly to the ^{14}C oxalic acid SRM 4990c radiocarbon standard. Significantly lower DPM indicates the presence of ^{14}C-depleted carbon. Zero percent ^{14}C, when compared to the standard, signifies the entire lack of ^{14}C atoms in a material, thus, indicating a petroleum-based carbon source. The bio-based content was calculated according to Equation 3.

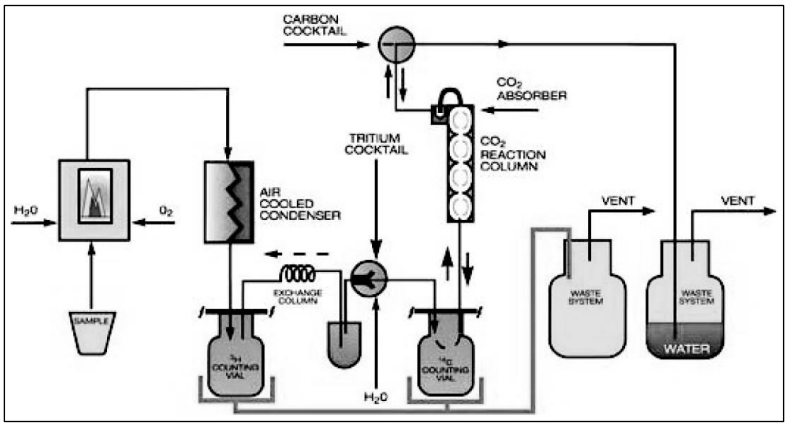

Figure 1. Flow diagram of sample preparation with the 307 Sample Oxidizer

$$Counting\ efficiency\ (\%) = \frac{Counts\ per\ minute\ (cpm)}{Disintegration\ per\ minute\ (dpm)} \times 100\% \quad (1)$$

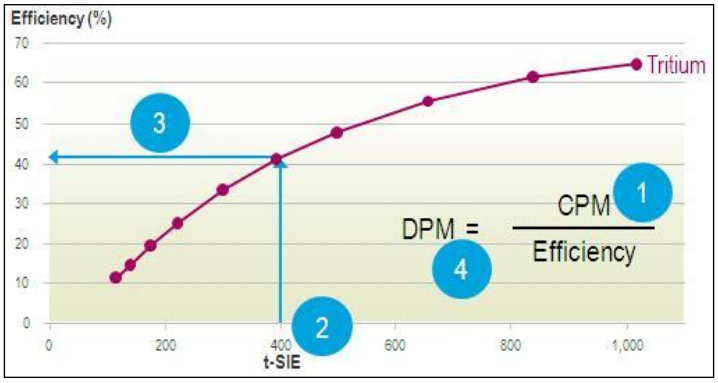

Figure 2. Usage of quench curve for determination counting efficiency and DPM

$$Disintegration\ per\ minute\ (dpm) = \frac{Counts\ per\ minute\ (cpm)}{Counting\ efficiency\ (\%)} \times 100\% \quad (2)$$

$$Bio - based\ content\ (\%) = \frac{dpm(sample)/weight(sample)}{dpm(reference)/weight(reference)} \quad (3)$$

Results and Discussion

Optimization of LSC and sample oxidizer

The minimum acceptable efficiency for ^{14}C in the range of 0-156 keV is 95% for PerkinElmer Tri-Carb 2910TR. Counting efficiency is a parameter measured as part of Instrument Performance Assessment. The performance of the LSC was assessed periodically *via* Self-Normalization and Calibration, where reference standards (^{14}C, ^{3}H and Background with known radioactivity (DPM) were counted and the counting efficiency was calculated. The counting efficiencies obtained for ^{14}C and ^{3}H were well above the minimum limit of 60% and 90%, respectively, as per the instrument's requirements specified by PerkinElmer.

The conditions of the Sample Oxidizer (amount of sample for combustion, time of combustion and amount of LSC cocktails) were investigated to find the optimum settings. The method was optimized using polyols instead of polyurethanes in order to minimize problems that may rise due to various components in polyurethanes.

Method validation

The combustion method was optimized for determination of bio-based content of palm-based polyols. Based on ICH Harmonised Tripartite Guideline Validation of Analytical Procedures: Text and Methodology Q2 (R1) (2005), this method was validated with respect to trueness (recovery and memory tests), linearity (quench curves) and precision (repeatability and interlaboratory comparison) using the optimized instrumental conditions. The quench curves, recovery and memory tests were performed with the ^{14}C Spec Chec standards.

The recovery of the method was tested by combusting a known activity of ^{14}C Spec Chec standards and those samples were compared with non-combusted samples with the same activity. The recovery (in %) was calculated using Equation 4 below.

$$Recovery\ (\%) = \frac{CPM_{combusted}}{CPM_{non-combusted}} \times 100\% \quad (4)$$

If samples with high activity were combusted, there is a possibility that some of the activities were retained in the Oxidizer and released when combusting the next samples. This is known as the memory effect, and it was investigated by combusting samples of a known activity of ^{14}C, followed by combusting an inactive standard sample after each active sample. The memory (in %) was calculated using Equation 5 below.

$$Memory\ (\%) = \frac{CPM_{inactive} - CPM_{background}}{CPM_{non-combusted}} \times 100\% \quad (5)$$

The recovery and the memory were determined in six replicates (Table 1). The average recovery was found to be 100.1 ± 1.5%, which is within the acceptable range of 85-110%. Therefore, it was decided that the method does not need correction for recovery. The memory was found to be 0.05 ± 0.03%, which is less than 0.1%. Therefore, the memory did not need to be corrected when measuring samples with normal environmental ^{14}C levels.

Construction of quench curves

The quench curve was constructed by preparing 7 calibration samples with different amounts of CarbosorbE (0, 2, 4, 6, 8, 9, 10 mL) and with the same amount of ^{14}C standard solution (82600 DPM). Each calibration sample was counted for 2 min. These samples were measured with LSC and the counting efficiency was recorded and plotted as a function of the external standard quenching parameter, tSIE (Table 2, Figure 3).

In addition to acting as CO_2 trapping agent, Carbosorb E also increases the chemical quenching effect in the scintillation cocktail. The effect of Carbosorb E amount in the scintillation cocktail was studied. Increasing the amount of Carbosorb E has reduced the CPM and thus, the counting efficiency (Table 3).

The repeatability of the method was determined by analysing four replicates of oxalic acid by the same analyst and using the same instrumentation. The resultant coefficient of variation obtained was 10.4%, which is considered as acceptable (< 15%).

Interlaboratory comparison was performed by sending two polyol samples, one commercial polyol and one of the synthesized polyols selected randomly, to an ISO 17025:2005 accredited laboratory in the US. The reported values of bio-based content were compared with the results of analyses done in MPOB on the same samples (Table 4). Cross check results with the accredited laboratory suggested that the sample oxidation method coupled with LSC is able to provide reliable results, comparable to the expensive AMS technique used by the accredited laboratory. The determination of bio-based content by AMS requires a large, expensive, and sophisticated instrument, which needs to be managed by a large research institute for its viable operation.

Table 1. Recovery and memory results for ^{14}C

Performance Parameter	Recovery (%)	Memory (%)
Sample 1	99.42	0.02
Sample 2	101.87	0.05
Sample 3	98.99	0.02
Sample 4	99.18	0.06
Sample 5	102.27	0.08
Sample 6	101.38	0.07
Average	100.09	0.05
Standard deviation	1.48	0.03

Table 2. Measured CPM and TSIE of 7 calibration samples with varying amount of Carbosorb E and with same amount of ^{14}C activity

Vial Label	Combustion Time (min)	Amount of CarboSorb E (mL)	Filter Paper (g)	Measured CPM	Injected Activity DPM	Counting Efficiency (%)	Measured tSIE
C0	0	0	0	69631	82600	84.3	794.7
C1	0.3	2	0.1	67783	82600	82.1	363.3
C2	0.3	4	0.2	71215	82600	86.2	321.3
C3	0.3	6	0.4	66132	82600	80.1	243.1
C4	0.5	8	0.6	65875	82600	79.8	197.5
C5	0.7	9	0.8	64142	82600	77.7	180.7
C6	1.0	10	1.0	60410	82600	73.1	162.7

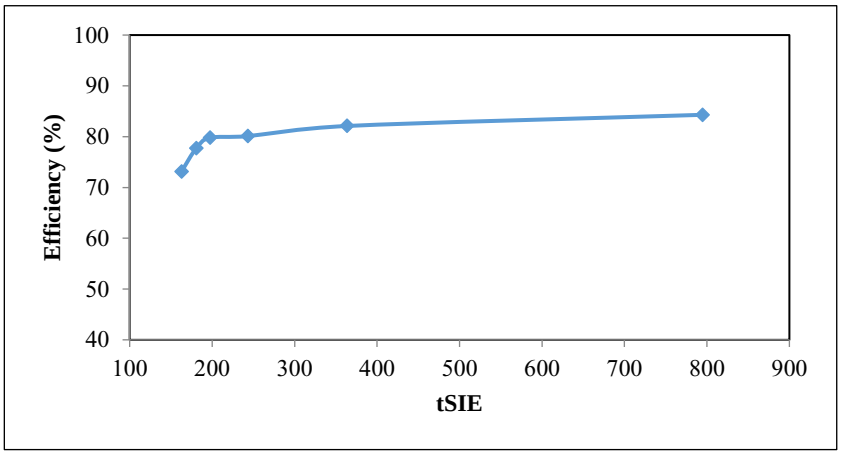

Figure 3. Quench curve for ^{14}C related to the usage of Carbosorb E

Table 3. Effect of Carbosorb E amount on CPM and counting efficiency

Carbosorb E (mL)	Measured CPM	Counting Efficiency (%)
0	69631	84.3
2	67783	82.1
4	71215	86.2
6	66132	80.1
8	65875	79.8
9	64142	77.7
10	60410	73.1

Table 4. Reported values of bio-based content by MPOB and an accredited laboratory on two polyol samples

Sample	Bio-based Content (%)	
	MPOB	Accredited Laboratory (US)
PolyFAME Bio PDO	100	98
Commercial polyol	85	89

Analyses of samples

A number of vegetable oils and polyols derived from vegetable oils were analysed to determine the bio-based content. The suitable amount (weight) of sample to be combusted was different for each sample. The weight ranged from 0.05 to 0.1 g. The amount of sample that gave counting efficiencies of 75% or higher was used to determine the bio-based content. The bio-based content was calculated according to Equation 3 and the results are tabulated in Table 5. NIST standard reference material 4990C (oxalic acid) was used as a reference.

The bio-based content of vegetable oils (palm oil, palm olein, coconut oil, canola oil, soybean oil, olive oil, sunflower oil and castor oil) was 100%. Most of the vegetable oils generally have 100% ^{14}C, which signifies an entirely modern carbon source, *i.e.* plants [13, 23]. Lower percent indicates the presence of ^{14}C-depleted carbon, which is likely to be fossil carbon source, *i.e.* petroleum.

The bio-based content of castor oil-based polyols (HCO-25, CO-25 and CO-5) ranged from 70 to 100%. HCO-25 and CO-25 have lower bio-based content, which can be due to their higher ethylene oxide degree (25 EO) compared to 5 EO for CO-5. Ethylene oxide used in the ethoxylation process is conventionally produced from fossil (petroleum) carbon source. The incorporation of ethylene oxide in the castor oil-based polyols have reduced the bio-based content.

For palm-based polyols (POoP M, POoP E135, POoP PG, POoP PDO, POoP PTDO and POoP HDO), the bio-based content ranged from 81 to 96%. The addition of reactants for ring-opening reaction of EPOo has consequently lowered the bio-based content of the resulting polyols compared to the bio-based content of EPOo and palm oil. All of the reactants, *i.e.* methanol, 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, bio-based 1,3-propanediol, 1,5-pentanediol and 1,6-hexanediol, are from fossil carbon source. Meanwhile, POoP Bio PDO had 100% bio-based content. This result is expected since the reactant (Susterra® 1,3-propanediol) used for ring-opening is also 100% bio-based.

For FAME-based polyols (PolyFAME PDO, PolyFAME BDO, PolyFAME PTDO and PolyFAME HDO), the bio-based content ranged from 71 to 74%. The addition of reactants for ring-opening reaction of E-FAME has consequently lowered the bio-based content of the resulting polyols compared to the bio-based content of E-FAME. All of the reactants are from fossil carbon source. Meanwhile, PolyFAME H had 100% bio-based content due to the addition of water, which did not contribute any carbon to the resulting polyol. PolyFAME Bio PDO had 100% bio-based content. This result is expected since the reactant (Susterra® propanediol) used for ring-opening is also 100% bio-based.

Interestingly, POoP Bio PDO and POoP PDO share the same chemical structure, yet they have significantly different bio-based content. Both polyols showed comparable glass transition temperatures, crystallinity and melt temperatures [7]. Similar findings were also observed on PolyFAME Bio PDO and PolyFAME PDO, whereby the reactants (bio-based Susterra® 1,3-propanediol and 1,3-propanediol, respectively) did not have an impact on their thermal crystallinity [5].

Overall, the presented results showed that the determination of bio-based content of products can be estimated using LSC analysis of ^{14}C cocktails with great confidence, as reported by others worldwide [17, 24-28]. It is also noteworthy to mention that this method offers reliable results at inexpensive costs which will benefit bio-based material producers in promoting the production of biomass-based products in the commercial market.

Table 5. Measured DPM, weight and calculated bio-based content of reference, vegetable oils, castor oil-based polyols, palm-based polyols and FAME-based polyols

Sample	**DPM**	**Weight (g)**	**Biobased Content (%)**
Reference	83	0.1099	-
Vegetable oils			
RBDPO	54	0.0547	100
RBDPOo	59	0.0501	100
Canola oil	73	0.0500	100
Soyabean oil	53	0.0519	100
Olive oil	76	0.0497	100
Sunflower oil	70	0.0802	100
Castor oil	87	0.1105	100
FAME (Methyl oleate)	59	0.0506	100
Castor oil-based polyols			
HCO-25	56	0.1052	70.5
CO-25	70	0.1048	88.4
CO-5	78	0.0849	100
EPOo	168	0.1067	100
POoP M	75	0.1099	90.4
POoP E135	69	0.1085	84.2
POoP PG	56	0.0804	92.2
POoP PDO	74	0.1082	90.6
POoP Bio PDO	86	0.1002	100
POoP PTDO	73	0.1005	96.2
POoP HDO	62	0.1010	81.3
Commercial polyol	67	0.1049	84.6
FAME-based polyols			
E-FAME	85	0.1096	100
PolyFAME H	90	0.1001	100
PolyFAME PDO	55	0.1006	72.4
PolyFAME Bio PDO	77	0.1010	100
PolyFAME BDO	58	0.1052	73.0
PolyFAME PTDO	55	0.1019	71.5
PolyFAME HDO	56	0.1005	73.8

Conclusion

A radiocarbon technique, involving combustion of samples and counting of the resulting ^{14}C isotope, was successfully developed for the determination of bio-based content of polyols derived from palm oil. The parameters of the Sample Oxidizer, *i.e.* amount of sample for combustion, time of combustion and amount of LSC cocktails, were optimized in order to provide sufficient amount of ^{14}C in the form of LSC cocktails. The cocktails were then analysed using LSC to give the ^{14}C radioactivity and subsequently, the bio-based content of the samples.

The optimized method was validated with respect to trueness (recovery and memory tests), linearity (quench curves) and precision. Recovery tests using ^{14}C standard verified the performance of Sample Oxidizer and Liquid Scintillation Counter. The quench curve for ^{14}C was constructed to take into account chemical quenching effects. A number of vegetable oils and polyols derived from the vegetable oils were analysed using the validated method to determine their bio-based content. All of the vegetable oils have 100% ^{14}C, which signifies an entirely modern carbon (biomass) source. Polyols derived from castor oil, palm oil and FAME had lower bio-based content compared to their respective oils. This is due to the addition of reactants, which are from fossil carbon source. This method, based on LSC analysis of ^{14}C cocktails, can be used as a tool to determine the bio-based content of palm-based polyols. It has been proven to be able to provide reliable results and is comparable to the more expensive AMS technique.

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