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AN EXPERIMENTAL DESIGN APPROACH FOR THE ANALYSIS OF LIQUID PHASE PRODUCTS IN WATER FOR HYDROGENOLYSIS OF GLYCEROL USING IMMERSED SOLID-PHASE MICROEXTRACTION

(Pendekatan Reka Bentuk Eksperimen Untuk Analisis Produk Fasa Cecair Dalam Air Bagi Tindak Balas Hidrogenolisis Gliserol Menggunakan Rendaman Mikroekstraksi Fasa Pepejal)

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Abstract

In this study, a response surface methodology (RSM) was applied to optimize the immersed-solid-phase microextraction (immersed-SPME) conditions for the first time using a polyacrylate (PA) coated fiber. This was to determine liquid phase compounds in water for hydrogenolysis reaction of glycerol. There are a three-factor response surface experimental design was used to evaluate the interactive effects of extraction temperature (30-70 ºC), extraction time (10-30 minutes) and desorption time (2-18 minutes) on the analysis of liquid phase compounds in water for hydrogenolysis of glycerol using immersed-solid-phase microextraction (immersed-SPME). The extraction conditions using immersed-SPME were optimized in order to achieve high enrichment of the analytes from aqueous samples. The isolated compounds from the SPME fiber were desorbed and separated on a capillary polar column of a gas chromatography-flame ionization detector (GC-FID). The extraction time and desorption time were found significant in increasing the amount of glycerol in aqueous hydrogenolysis of glycerol. Nevertheless, the effect of extraction temperature was not significant. In terms of interactions between the effects, the relation between extraction temperature and extraction time was the most significant. The optimised immersed-SPME conditions were at extraction temperature of 27 °C, extraction time of 30 minutes and 15 minutes of desorption time. Thus, the application of SPME was found to be a rapid and effective technique in the determination of glycerol and propylene glycol compounds in aqueous hydrogenolysis glycerol.

Keywords: Solid phase microextraction (SPME), Hydrogenolysis ,Glycerol, Response Surface Method (RSM)

Abstrak

Dalam kajian ini, kaedah permukaan respon telah digunakan buat pertama kalinya untuk mengoptimumkan keadaan operasi teknik rendaman mikroekstraksi fasa pepejal menggunakan fiber poliakriat (PA). Teknik ini digunakan bagi menentukan komponen dalam fasa cecair dalam air bagi tindak balas hidrogenolisis gliserol. Terdapat tiga faktor reka bentuk permukaan respon yang digunakan untuk menilai kesan interaksi suhu ekstraksi (30-70 °C), masa ekstraksi (10-30 minit) dan masa penyahjerapan (2-18 minit) terhadap analisis komponen fasa cecair dalam air untuk hidrogenolisis gliserol dengan menggunakan teknik rendaman mikroekstraksi fasa pepejal (rendaman-SPME). Keadaan ekstraksi rendaman-SPME perlu dioptimumkan bagi mendapatkan serapan analit yang maksimum daripada sampel akuas. Komponen daripada fiber SPME ternyahjerap dan di pisahkan menggunakan kolum polar kapilari gas kromatografi yang dilengkapi dengan pengesan pengionan nyala (GC-FID). Kajian ini menunjukkan bahawa faktor masa ekstraksi dan masa penyahjerapan adalah signifikan dengan pertambahan amaun gliserol dalam hidrogenolisis gliserol berakuas. Namun begitu, kesan suhu ekstraksi didapati tidak siginifikan. Dari segi interaksi antara faktor, hubungan antara suhu ekstraksi dan masa ektraksi adalah yang paling signifikan. Keadaan optimum teknik rendaman-SPME adalah pada suhu ekstraksi 27°C, masa ekstraksi 30 minit dan masa penyahjerapan 15 minit. Oleh itu, didapati aplikasi SPME yang cepat dan teknik yang berkesan dalam penentuan komponan gliserol dan propilena glikol dalam hidrogenolisis gliserol berakuas.

Kata kunci : Mikroekstraksi fasa pepejal (SPME), Hidrogenolisis, Gliserol, Kaedah permukaan respon (RSM)

Introduction

Hydrogenolysis of biomass-derived glycerol is an alternative route to sustainable production of propylene glycol. Glycerol is the main by-product of biodiesel production by the transesterification of vegetable oils and animals fats [1]. Recently, rapid development of biodiesel processes has caused some concern over the oversupply of glycerol in the market [2]. A variety of valuable chemicals can be produced from glycerol [3]. Propylene glycol or 1,2-propanediol is an important commodity chemical. It is used as biodegrable functional fluids such as de-icing reagents, antifreezes and coolants and as precusors in the synthesis of unsaturated polyester resins and pharmaceuticals [4-6].

Gas chromatogaraphy-flame ionization detector (GC-FID) [3, 5, 7] and high performance liquid chromatogarphy (HPLC) [8], are widely used to determine glycerol and liquid products in water for glycerol hydrogenolysis. However, a preconcentration step prior to the chromatogaraphic analysis is necessary in order to achieve the low levels that are presents in real samples. Recently, a new extraction technique, solid-phase microextraction (SPME) was used as an alternative to conventional techniques. SPME is a screening technique introduced by Arthur and Pawlisyn in 1990 [9]. It acts as a modern alternative to traditional sample preparation technology, is able to address many of the requirements put forward for analytical research. It has attracted great attention and is now widely accepted as a reliable technique. There are several advantages that can be pointed out in relation to this technique, such as it is solvent free, fast and uses the whole sample for analysis. Furthermore, its requires only small amounts of sample and the fibers are highly reuseable. Accordingly, it has been successfully applied for the analysis of diverse organic compounds from different matrices[10-12].

To the best of our knowledge, there is no report on the technique to extract the liquid products and glycerol in water phase for glycerol hydrogenolysis. Therefore, in this study, the possibility of using SPME coupling with GC-FID for the analysis propylene glycol and glycerol in aqueous media was proposed. A direct immersed solid-phase microextraction (immersed-SPME), combined with the gas chromatography-flame ionization detector (GC-FID), was developed and applied to detect the compounds in water medium for hydrogenolysis of glycerol. Up until now, no references have been found on the use of immersed-SPME to describe the extraction technique of compounds for hydrogenolysis of glycerol in aqueous media. Therefore, to optimize the extraction conditions, a response surface experimental design was set up to analyze the effect of three factors: extraction temperature, extraction time and desorption time. Finally, the developed method is applied to the real samples for glycerol hydrogenolysis reaction.

Experimental

Standard solution

A mixture of standard solution containing propylene glycol, ethylene glycol and glycerol with approriate concentration were prepared and this mixture was then used in order to optimize SPME condition using a face-centered central composite design.

Chemicals

Glycerol, 1,2-propanediaol (1,2-PDO) or propylene glycol and ethylene glycol (EG) were purchased from Sigma-Aldrich (Steinheim, Germany). Next, 1,4-butanediol and n-butanol were used as internal standard and these were obtained from Merck (Darmstadt, Germany).

Qualitative characterization of the isolated compounds

Qualitative analysis for liquid phase of hydrogenolysis was performed on Hewlett Packard Gas Chromatograph HP 6890 Series II Plus equipped with a flame ionization detector (FID). The column used was DB-WAX capillary column, 30 m x 0.25 mm and 0.25 μm film thickness from J & W Scientific (Pennsylvania,USA). The GC temperature and condition were as follows : initial temperature started at 45°C held for 5 minutes and increased to 250°C and held for 3 minutes with temperature ramping of 3°C min^{-1}; splitless injection port temperature at 250°C; detector temperature 280°C; carrier gas (helium) at a flow rate of 1.7 ml min^{-1}. The injector port was equipped with a glass liner designed for SPME measurement (0.75 mm i.d. splitless glass liner, Supelco). The GC-FID was used for the optimization of the direct immersed SPME method and quantification of 1,2-PDO from hydrogenolysis of glycerol.

SPME fiber

SPME extractions were performed using 80 μm polyacrylate fiber and it was purchased from Supelco, Bellefonte, Pennsylvania, USA. The selection of this fiber was made due to its polarity and relatively high thickness. The fiber was conditioned in a gas chromatograph injection port at 250°C to remove fiber contaminants as recommended by the manufacturer.

Extraction and analysis of liquid products

A direct immersed solid phase microextraction (immersed-SPME) was employed in the extraction of samples in water for glycerol hydrogenolysis. After the reaction, the liquid phases were separated with a solid catalyst using a centrifuge at 4000 rpm for 15 min. Then, the liquid phases were filtered to remove other impurities. Finally, the liquid phases were poured into 4 ml vial for SPME extraction procedure.

After optimization, and for each SPME analysis, a volume of 4 mL of sample was placed into a 4 mL glass vial. Each sample was spiked with about 0.1 g of internal standard solution. A small magnetic stirring bar (0.8 cm x 0.2 cm) was used to mix the solution. The vial was tightly capped with a PTFE-faced silicone septum and was placed in a thermostat block on a stirrer. The sample was equilibrated for 5 minutes at sampling temperature and, after this, the SPME fiber was directly immersed in the sample. During the extraction, the sampling was stirred at constant speed (300 rpm). Upon completion of the extraction, the SPME fiber was removed from the sample vial and was placed immediately into the injection port of GC for 10 min for analysis.

Experimental Design

The Response Surface Methodology (RSM) was used as it allowed the evalution of the effects of many explanatory variables and their interactions on the response variable [13]. It also enabled one to make a reduction in the number of experiments and yet provided sufficient information for statistically acceptable results for evaluating the effect of multiple explanatory variables, alone or in a combination, on response variables [14, 15]. RSM has been used widely in research particulary for the optimization of conditions and processes[16].

In order to optimize the parameters, the response surface approach was used by using a set of experimental design was performed. A central composite design with five coded levels was applied with three experimental variables (factors), namely extraction temperature, extraction time and desorption time. This design was selected because it required four additional points outside the range which could extend this model to a wider range of variation to include the highest and the lowest value of the independent variables. The independent variables were the extraction temperature (A) , extraction time (B) and desorption time (C). The range for the independent variables was (low/high value): extraction temperature (°C), 30/70, extraction time (minutes), 10/30, and desorption time (minutes), 2/18. A set of 20 experiments was carried out. The coded levels and values of the factors set in this experiment are shown in Table 1. The response variables selected were gas chromatography area count for glycerol, 1,2-propanediol and ethylene glycol. Six replications were performed at centre point. The design matrix of the centre composite design is shown in Table 2. The order of these experiments was randomized to remove any systematic error.

Table 1. Coded level and values of the design factors

Levels	Extraction temperature (°C)	Extraction time (min)	Desorption time (min)
$-\alpha$	30	10	2
-1	40	15	5
0	50	20	10
1	60	25	15
$+\alpha$	70	30	18

The results were analyzed by Statistical software package Design Expert 6.0.6, an expert system for the design and analysis of experiments. The model permitted evaluation of the effects of linear, quadratic and interactive terms of the independent variables on the dependent variables. Three–dimensional surface plots were drawn to illustrate the main and interactive effects of the independent variables on glycerol hydrogenolysis. The optimum values of the selected variables were obtained by solving the regression and also by analyzing the response surface contour plots.

Results and Discussion

Direct immersed extraction and identification of liquids products using GC-FID

The immersed solid phase microextraction of the liquid products was directly extracted onto the SPME fiber which was later analyzed using GC-FID. This analytical method allows one to make correct identification of compounds in water. Fig. 1(A) shows a chromatogram of standard solution containing glycerol, 1,2-PDO and EG detected by GC-FID. The retention time of glycerol, 1,2-PDO and EG were 50.3 min, 26.9 minutes and 28.2 minutes respectively.The GC-FID chromatogram of liquid sample was shown in Fig. 1(B) and the retention time of the glycerol, 1,2-PDO and EG compounds was quite similar with rentention time in standard solution. Generally, these two samples could be separated well with high resolution separation. As for quantification analysis, the retention time of 8.1 min and 39.2 min corresponding to n-butanol and 1,4-butanediol was used as internal standard.

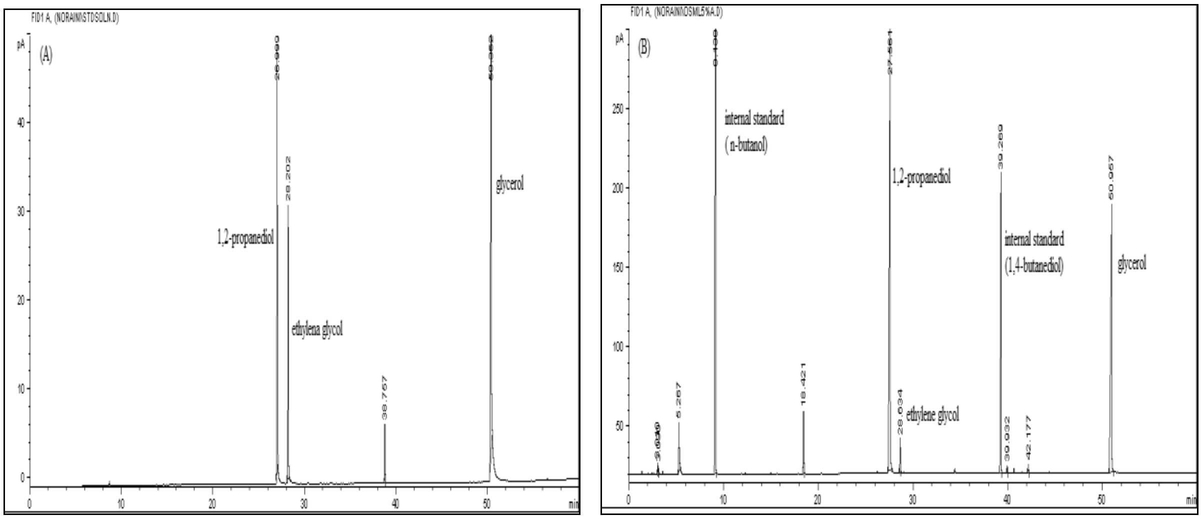

Figure 1. GC chromatogram of standard solution (A) and liquid phase sampel in hydrogenolysis of glycerol detected by GC-FID (B)

Optimization of SPME fiber for the extraction of glycerol and liquid products by RSM

The amount of analyte extracted by solid-phase microextraction could be influenced by several factors including fiber type, extraction time, extraction temperature, salt concentration, sample pH, sample volume, agitation rate, etc [16, 17]. It is well known that among these factors extraction temperature, extraction time and desorption time played the most important role in the extraction process. In this study, these three factors were therefore chosen and optimized. Traditional methods of optimization could evaluate the effect of one variable at a time, keeping all the others constant during experiments with the exception of the one being studied. However, this type of experiment does not allow one to determine what would happen if the other variables also changed. The experimental design enabled the effect of several variables to be estimated simultaneously. In particular, response surface methodology coupled with a central composite design was an effective tool for optimizing a process [18] and was therefore applied in this study.

Optimization is an important process because the immersed-SPME method is based on the principle of equilibrium. The SPME fiber will reach equilibrium with a compound at a certain time and temperature. The maximum absorption of glycerol and liquid products on the SPME fiber was optimized as it represents the equilibrium point of the compound with the fiber. RSM was applied to the immersed solid-phase microextraction of glycerol and liquid products in water from glycerol hydrogenolysis with two absorption parameters: time and temperature and desorption time as well. Table 2 lists the peak area of glycerol, 1,2-PDO and EG in each of the 20 experiment sets generated by the RSM software.

Table 2. Central composite design and experimental data for the extraction of glycerol and liquid products in water from glycerol hydrogenolysis via immersed-SPME-GC-FID

Run Order	Block	Independent variables			Response 1 Glycerol GC area	Response 2 1,2-PDO GC area	Response 3 EG GC area
		A (°C)	B (min)	C (min)			
1	1	27.00	10.00	5.00	2223.03	2269.25	1685.07
2	1	70.00	10.00	15.00	3417.48	2026.77	1562.05
3	1	27.00	30.00	15.00	7385.06	5017.2	3856.89
4	1	70.00	30.00	5.00	3604.43	3128.22	2298.06
5(C)	1	48.50	20.00	10.00	5607.48	5019.29	3578.48
6(C)	1	48.50	20.00	10.00	4505.25	3963.45	2985.67
7	2	27.00	10.00	15.00	3261.88	2515.85	1872.52
8	2	70.00	10.00	5.00	3546.22	3753.00	2684.73
9	2	27.00	30.00	5.00	4006.14	3336.97	2456.30
10	2	70.00	30.00	15.00	4452.05	2757.43	2178.12
11(C)	2	48.50	20.00	10.00	4257.46	3391.63	2469.5
12(C)	2	48.50	20.00	10.00	4038.06	2732.30	3806.61
13	3	12.34	20.00	10.00	1457.71	1665.63	1177.52
14	3	84.66	20.00	10.00	2286.51	1732.46	1320.03
15	3	48.50	3.18	10.00	1938.41	1938.58	1389.83
16	3	48.50	36.82	10.00	3020.82	2681.56	1930.79
17	3	48.50	20.00	1.59	1340.28	1311.64	927.61
18	3	48.50	20.00	18.41	2831.95	2648.83	1924.86
19(C)	3	48.50	20.00	10.00	2224.62	1988.92	1427.63
20(C)	3	48.50	20.00	10.00	2422.64	2103.88	1508.98

The six center points as shown in Table 2 produced four measures of variation known as pure error. There were four measures of variation due to the use of a block as the optimization could not be performed within the same day. Pure error represented the replication error and it was used in evaluation for the lack of fit. The significance of the equation parameters for each response variable was assessed by F-ratio at a probability (p) of 0.05. The closer the value of R^2 to unity, the better the empirical model fitted the actual data. The fit of the RSM model was evaluated by coefficients of determination (R^2) and a test for lack of fit from ANOVA (Table 3a-c). The quadratic model is significant with a *p*-value of 0.0146 ($p < 0.05$) and the model has no lack of fit at 95% confidence level. The R^2 value of 0.8548 (Table 3a) and the observed values versus predicted values plot (Fig. 2) shows that the model is statiscally acceptable. This indicates that the model could explain 85.48% of the variability in the response. According to Bogusz and Tavares [16], the R^2 should be at least 0.80 for a good fit of a model.

Table 3a . ANOVA for response surface quadratic model for Response 1 (glycerol)

Source	Response 1 (glycerol)				
	SS	*df*	MS	*F* value	*p* value
Block	2.008E+007	2	1.004E+007		
Model	1.725E+007	9	1.916E+006	5.23	0.0146
A- Extraction Temp	1.563E+004	1	1.563E+004	0.043	0.8415
B – Extraction Time	5.696E+006	1	5.696E+006	15.55	0.0043
C – Desorption Time	4.280E+006	1	4.280E+006	11.68	0.0091
A^2	9.322E+005	1	9.322E+005	2.54	0.1493
B^2	2.263E+004	1	2.263E+004	0.062	0.8100
C^2	4.602E+005	1	4.602E+005	1.26	0.2949
AB	2.896E+006	1	2.896E+006	7.91	0.0228
AC	1.710E+006	1	1.710E+006	4.67	0.0627
BC	1.375E+006	1	1.375E+006	3.75	0.0887
Residual	2.930E+006	8	3.663E+005		
Lack of fit (model error)	2.279E+006	5	4.559E+005	2.10	0.2874
Pure error (replicate error)	6.511E+005	3	2.170E+005		
Corrected total	4.025E+007	19			
R^2	0.8548				

Table 3b . ANOVA for response surface quadratic model for Response 2 (1,2-PDO)

Source	Response 2 (1,2-PDO)				
	SS	*df*	MS	*F* value	*p* value
Block	9.044E+006	2	4.522E+006		
Model	7.975E+006	9	8.861E+005	2.11	0.1532
A- Extraction Temp	1.357E+005	1	1.357E+005	0.32	0.5853
B – Extraction Time	1.776E+006	1	1.776E+006	4.23	0.0738
C – Desorption Time	3.164E+005	1	3.164E+005	0.75	0.4107
A^2	9.830E+005	1	9.830E+005	2.34	0.1645
B^2	29479.07	1	29479.07	0.070	0.7977
C^2	3.773E+005	1	3.773E+005	0.90	0.3710
AB	1.499E+006	1	1.499E+006	3.57	0.0955
AC	2.024E+006	1	2.024E+006	4.82	0.0594
BC	9.724E+005	1	9.724E+005	2.32	0.1666
Residual	3.359E+006	8	4.199E+005		
Lack of fit (model error)	2.578E+006	5	5.156E+005	1.98	0.3046
Pure error (replicate error)	7.814E+005	3	2.605E+005		
Corrected total	2.038E+007	19			
R^2	0.7036				

Table 3c . ANOVA for response surface quadratic model for Response 3 (EG)

Source	Response 3 (EG)				
	SS	*df*	MS	*F* value	*p* value
Block	6.565E+006	2	3.283E+006		
Model	5.463E+006	9	6.070E+005	2.19	0.1414
A- Extraction Temp	5.907E+004	1	5.907E+004	*0.21*	0.6565
B – Extraction Time	1.105E+006	1	1.105E+006	*3.99*	0.0808
C – Desorption Time	2.966E+005	1	2.966E+005	*1.07*	0.3310
A^2	1.044E+006	1	1.044E+006	3.77	0.0881
B^2	2.206E+005	1	2.206E+005	*0.80*	0.3981
C^2	6.143E+005	1	6.143E+005	*2.22*	0.1747
AB	9.945E+005	1	7.914E+005	*2.86*	0.1294
AC	6.082E+005	1	9.945E+005	*3.59*	0.0947
BC	2.215E+006	1	6.082E+005	*2.20*	0.1766
Residual	1.142E+006	8	2.769E+005		
Lack of fit (model error)	1.142E+006	5	2.285E+005	0.64	0.6920
Pure error (replicate error)	1.073E+006	3	3.577E+005		
Corrected total	1.424E+007	19			
R^2	0.7115				

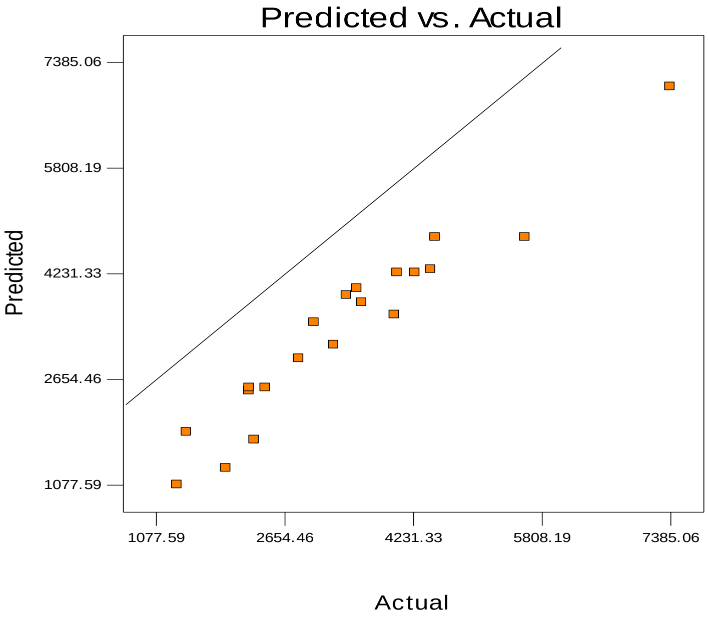

Figure 2**.** Plot to show relationships between observed values and values predicted by the model

It was found that for the recovery of glycerol at the 95% confidence level (Prob > F was less than 0.05), three parameters (extraction time (B), desorption time (C) and interaction between extraction temperature and extraction time (AB), were significant. However, no variables were significant for the recovery of 1,2-PDO and EG. Therefore, only glycerol was used to optimize the extraction of glycerol and liquid products in water for hydrogenolysis glycerol reaction. In this study, the response and explantory variables were fitted to each other by RSM. A good fit was obtained and there were no outliers observed for the quadratic model:

Peak area of glycerol = $-3799.2 + 150.79A + 133.26B + 287.76C - 0.550A^2 - 0.396B^2 - 7.151C^2 - 2.798AB - 4.30BC$

Figure 3 illustrated the relationship between the explanatory and response variables in a three-dimensional representation of the response surface and two-dimensional contour plot generated by the model. It was observed that the peak area of glycerol increased in a quadratic manner with the extension of time at room temperature. It was noted that there was an effect of interaction between the extraction time and the temperature on the peak area of glycerol.

A numerical optimization was also carried out using the Design-Expert software to determine the optimum extraction parameter (time and temperature) and desorption time of the SPME fiber for the maximum extraction of glycerol. Results showed that the estimated optimum values for extraction temperature and time and desorption time by response surface methodology were 27°C, 30 min and 15 min, respectively. To evaluate the accuracy of the results obtained by the response surface model, four experiments were carried out under the optimum conditions. Results showed, there was a good agreement between the calculated and experimental responses (Table 4).

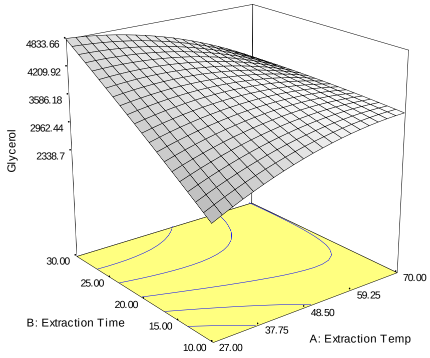

Figure 3. Response surface and contour plot for the effects of extraction time and temperature on the peak of glycerol

Table 4. Optimum response and the corresponding levels

Extraction Temperature (°C)	Extraction Time (min)	Desorption Time (min)	Optimum response (Total area)	Experimental response[a] (Total area)
27	30	15	11 072.76	10 987. 35

[a] Mean value of the measurement (n = 4)

For comparative purposes, the traditional one-at-a-time technique was also used to find the optimum conditions. Only extraction temperature was the same level as the experimental design method, except for extraction time, which was 30 minutes instead of 5.0 minutes and desorption time, which was 15 minutes instead of 10 minutes,. This might be due to the fact that the response surface model had more linear than non-linear characteristics. However, to reach the optimum conditions, much fewer experiments were needed in the experiment design compared to the one-at-a-time technique.

Analysis of Liquid Products Sample From Hydrogenolysis of Glycerol

The optimized extraction conditions (extraction temp = 27°C, extraction time = 30 minutes and desorption time = 15 minutes) were then applied in analyzing real liquid samples for glycerol hydrogenolysis reaction. The two chromatograms showed a similar paterrn for retention time from 2 to 50 minutes (Figure not shown). However, the GC-FID chromatogram showed quite different peak areas for glycerol, 1,2-PDO and EG before and after optimizing the SPME conditon (Table 5). This indicated that the optimum condition obtained using RSM gave the highest extraction of compounds in water for hydrogenolysis of glycerol.

Table 5. Peak area of glycerol, 1,2-PDO and EG compounds in water before and after optimization

Retention time (min)	Compound	Peak area analyze by GC-FID	
		Before Optimum[a]	Optimum Condition
50.6	glycerol	1450.14	2698.02
27.2	1,2-PDO	1951.06	2534.31
28.2	EG	78.94	112.51

[a] extraction temperature = 27°C, extraction time = 5 min , desorption time = 10 min

Conclusion

In this study, the effect of three operating parameters of solid phase microextraction (SPME), namely extraction temperature, extraction time and desorption time on the extraction of 1,2-propanediol and glycerol in water were evaluated using an experimental design based on central composite design approach. The optimized operating conditions for the extraction were identified using a response surface method. Consequently, this study proved that SPME coupled with GC-FID was able to provide a fast, simple and solvent-free method for the analysis of liquid products in aqueous phase glycerol hydrogenolysis reaction.

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