Research Article

Application and Process Development of Microwave Radiation for Etherification of Glycerol to Value-Added Polyglycerols

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Abstract

Glycerol is a cost-effective, renewable and environmentally friendly chemical building block, that can be converted into various valuable chemicals. Recently, the rapid increase in the amount of glycerol generated as by-product from the biodiesel production has significantly decreased the glycerol price. This study demonstrated the feasibility to scale up the etherification of glycerol to polyglycerols using microwave radiation, from a small laboratory microwave reactor to a larger scale (100X) in an inexpensive commercial microwave oven. A vacuum distillation was used to improve the purity of the desired polyglycerols to a commercial grade. In this developed process, glycerol was the only reactant without solvent, and microwave radiation was utilized as a heat source. The microwave radiation allows an efficient heating of the large-scale reactions in a shorter period of time, which has a tremendous impact on the cost of the process. The scale up development was done at 1 kg scale, 230 °C, 1000 W, 1.5 h, and with 3 wt% of Na_2CO_3 as a catalyst. The conversion, the combined yield (diglycerols, triglycerols, and tetraglycerols), the selectivity toward pentaglycerols, and the selectivity toward cyclic diglycerols are 84, 71, 11, and 4 percent, respectively. An increase in reaction time and temperature resulted in the formation of undesirable cyclic diglycerols and bigger polyglycerols. Furthermore, after vacuum distillation at 200 °C, the unreacted glycerol and cyclic diglycerols were efficiently removed. The compositions of the desired polyglycerols were vastly improved to nearly 100%. HPLC, ^{1}H-NMR, ^{13}C–NMR, and mass spectrometry were used to quantitatively and qualitatively analyze the polyglycerol products.

Keywords: Glycerol; Oligoglycerols; Microwave-assisted Etherification;
Scale up of glycerol etherification; Distillation of polyglycerols mixture.

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1. Introduction

Current demands for energy has increased due to industrialization and population boom while petroleum sources are diminishing. With the prediction about the depletion of petroleum oil reserves, many studies focus on the utilization of renewable resources. Biodiesel is a key renewable energy source to replace fossil fuels. Biodiesel along with glycerol by-product are generated from trans-esterification of vegetables or animal oils [1]. Approximately, 100 kg of glycerol (1,2,3-propanetriol) by-product is generated per ton of biodiesel produced [2]. Biodiesel production is dramatically increasing every year, resulting in an oversupply of glycerol. Consequently, the glycerol price has dropped significantly. The low cost of glycerol has turned it into one of the most promising platform chemicals for a sustainable future [3]. Therefore, the utilization of the low-valuable glycerol as a starting material for more advanced chemicals has been of great industrial importance because glycerol is a nontoxic and renewable compound [4]. There are many useful products that can be derived from glycerol such as acrolein, glyceric acid, glycerol carbonate, and 1,3-propanediol [5]. Relying on an etherification process, glycerol is also a suitable starting material for the synthesis of oxygenated polyglycerol compounds [4].

Our focus is on the etherification of glycerol to polyglycerols, especially diglycerols (DG), triglycerols (TG), and tetraglycerols (TtG) because they are useful chemicals for several industries including pharmaceutical, cosmetics, food, and polymers industries [4]. The market for polyglycerols is promising, but challenges in the production process still remain. Commercially, diglycerols are produced by the base hydrolysis of epichlorohydrin using NaOH or Na_2CO_3 solution [6]. Epichlorohydrin is obtained from the reaction between glycerol and hydrochloric acid (HCl) in the Epicerol® process. Drawbacks of this process are the need for multiple reaction steps, the presence of epichlorohydrin as a carcinogenic intermediate, and the need for fractional distillation to remove residual glycerol and higher polyglycerols [7]. An alternative to the commercial process of polyglycerols is the glycerol etherification at elevated temperature over acid or base catalysts [7, 8]. The main advantage is that it only requires one reaction step to obtain the polyglycerol products. Therefore, the production process is less complicated and more efficient. Etherification of glycerol has been studied widely. The types of catalysts and reaction conditions are important parameters, that have been investigated to achieve the highest selectivity toward the desired products with the possible highest conversion of glycerol.

Consecutive etherifications of glycerol condense the molecules in linear, branched, or cyclic fashions to generatepolyglycerols. Both primary and secondary hydroxyls act as a nucleophile to attack a carbinol carbon either intermolecularly or intramolecularly. Both homogeneous and heterogeneous catalysts have been investigated for the glycerol etherification [9-12]. Homogeneous catalysts such as H_2SO_4, NaOH, Na_2CO_3, CsOH, and Cs_2CO_3 provide higher conversions but lower selectivity to the desired small oligosaccharides including DG and TG when compared with heterogeneous catalysts [13]. The yield and selectivity of the reaction depend on the basicity and solubility of the catalysts in glycerol. Alkali hydroxides are stronger bases but less soluble in glycerol than carbonates [8]. The alkali carbonates perform better in catalyzing the etherification of glycerol in a solvent free condition due to their superior solubility in glycerol [8]. Although heterogeneous catalysts can be separated from the reaction mixture and may be reused, major disadvantages including high cost, difficulty to prepare, leaching and solubility of chemicals, low thermal stability, and low surface area do exist [9-11]. In addition, higher temperatures and longer reaction times are often required in the reactions that employ heterogeneous catalysts.

Microwave heating has been used in many commercial scale applications of polymerizations, such as the polymerization of polymethylmetacrylate (PMMA), polymethylacrylate (PMA), and polystyrene (PS) [14]. The main advantages of microwave heating over conventional heating are shortened reaction time, reduced localized overheating, fewer side reactions, and subordinate thermal decomposition [15]. The mentioned advantages are due to the higher temperature homogeneity and rapid heating of microwave irradiation.

This work aims to demonstrate the feasibility of microwave radiation for the etherification of glycerol in a larger scale for the purpose of process development. The first part of the experiments was carried out using a microwave reactor in a small scale to screen for suitable reaction parameters in etherification of glycerol to generate polyglycerols without solvent. The second part of the experiment was done in a simple household microwave oven at a 1 kg scale. A distillation was used to improve the purity of the desired polyglycerols to a commercial grade level. The achievement of the highest combined yields of small polyglycerols, including diglycerols, triglycerols, and tetraglycerols, are preferred.

Polyglycerol products may be used as an additive in food applications. According to the Joint FAO/WHO Expert Committee on Food Additives (JECFA) specification of polyglycerols composition, polyglycerols in food additives can be a mixture of diglycerols, triglycerols, and tetraglycerols. The total amount diglyerols, triglycerols, and tetraglycerols in the mixture must be at least 70-75%. And the total amount of polyglycerols which are larger than hexaglycerols should not be more than 10% of the composition [16, 17].

In this study, sodium carbonate (Na_2CO_3) was the catalyst of choice in the process development because of its low cost compared to other metal carbonates, commercial availability, safety, and its high solubility in glycerol. In general, metal carbonate catalysts are more active than hydroxides because of their higher solubility in glycerol [7]. In addition, the base-catalyzed pathway of glycerol etherification can suppress the formation of undesirable cyclic oligomers and acrolein [18, 19]. The reaction parameters in this study were reaction temperature, reaction time, and catalyst concentration. The etherification of glycerol yields various types of polyglycerols as shown in Fig. 1 as well as different isomers of the undesired cyclic diglycerol (Fig. 2) [8].

High Performance Liquid Chromatography (HPLC) was used for quantitative analyses of polyglycerol products. The structures of the polyglycerol products were characterized by ^{1}H-NMR, ^{13}C-NMR, and high resolution mass spectrometry.

2. Methodology/Experimental Design

2.1 Experiment on a 10 g scale

Na_2CO_3 (Merck, Germany) was added to glycerol (10 g) in a 100 mL round-bottom flask. Glycerol etherification was conducted in a stirred microwave reactor, without additional solvent, under various conditions as follows: reaction temperature of 220 °C and 270 °C; 1 wt% and 3 wt% of catalyst concentrations; microwave power of 300 W, and pressure at 1 atm for 3 h. Sample collections were done at 0.5 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, and 3.0 h. In order to prevent evaporated water from re-entering the system, a bump trap and a condenser (25 °C) were connected to the glass reactor. The heat source is microwave irradiation provided by the open vessel mode of CEM Discover® SP operating at 2.45 GHz and 300 W maximum power output.

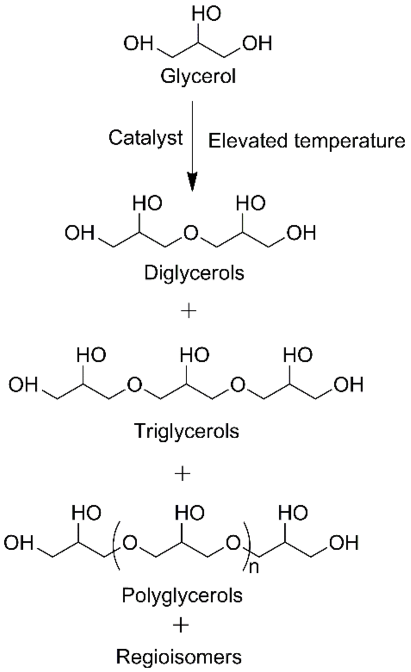

Fig.1. Catalytic etherification of glycerol to polyglycerols.

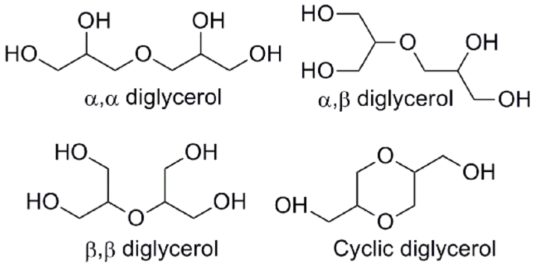

Fig.2. Possible isomers of diglycerols formed by etherification [8].

2.2 Experiments on a 1 kg scale

Na_2CO_3 (3 wt%, Merck, Germany) was added to 1 kg of glycerol in a 3000 liter Pyrex glass container (25 cm in diameter, 9 cm in height). Glycerol and Na_2CO_3 were initially mixed in a glass container. Glycerol etherification was carried out in a household microwave oven (Panasonic, NN-ST651M) without any stirrer. The reaction mixtures were not preheated. A constant microwave radiation was applied to the reaction mixture at room temperature. The reaction temperatures were ~ 230 °C (measured at the end of the reaction by an IR thermometer), without mechanical or magnetic bar stirring. The reaction time was 1 h to 3 h. The reaction was conducted by the microwave power of 1000 W and at atmospheric pressure. No additional solvent was added.

Products from the glycerol etherification were qualitatively characterized by electrospray ionization mass spectrometry (ESI-MS). ESI-MS analyses were conducted by the MS-service at Chulabhorn Research Institute (CRI, Bruker mass spectrometer). Peaks are reported as m/z with ionization of analytes by sodium cations. The compositions and yields of the products from the glycerol etherifications were determined by high performance liquid chromatography (HPLC, Agilent 1260 Infinity series). Octan-1-ol was used as an internal standard (2.5 μL/1 mL of prepared sample) for the calibration curve. Samples were collected after the elution of each analyte, and its identity was confirmed by ESI-MS, ^{1}H-NMR, and ^{13}C-NMR.

2.3 Vacuum distillation process

The vacuum distillation process was applied to the three selected crude products from three different reactions including 1) the crude mixture from the reaction conducted in the CEM microwave reactor using 300 W, 2) a crude mixture from a 1 kg scale at 1000 W of microwave power at 67.5 min, and 3) a crude mixture from a 1 kg scale at 1000 W of microwave power at 90 min.

The vacuum distillation process was conducted at 200 °C by Edwards RV5 high vacuum pump (ultimate pressure of 2 x 10^{-3} mbar). The results of the vacuum distillation were monitored by HPLC for the chemical contents of the purified products. The performance of the vacuum distillation was monitored over the distillation time.

2.4 MS and NMR analysis

All products were identified by high resolution mass spectrometry, ^{1}H- NMR, and ^{13}C–NMR. High resolution mass spectra were recorded with a micrOTOF instrument with source type of ESI. NMR spectra were recorded with a Bruker AVANCE III spectrometer (300 MHz for both ^{1}H and ^{13}C). Deuterium oxide (D_2O) was used as a solvent. The standard diglycerols (DG), triglycerols (TG), and tetraglycerols (TtG) were purchased from Merck, Germany and TCI, Japan. ^{1}H-NMR (D_2O) of a mixture of the standard compounds showed overlapped signals (δ) in the region of 3.40 to 3.85 ppm with multiple peaks. The ^{13}C-NMR peaks of a mixture of the standard compounds are the followings (^{13}C-NMR in D_2O): δ = 60.5 (C-7), 61.2 (C-9), 62.5 (C-1), 68.5 (C-11), 69.0 (C-10), 70.5 (C-2), 71.0 (C-4), 72.0 (C-3), 79.5 (C-6), 80.0 (C-8), 81.2 (C-5). There are four main regions of chemical shifts (δ) and their corresponding signals as follows: 1) 60-63 ppm from CH_2OH; 2) 68-70 ppm from -CHOH-; 3) 71-72 ppm from $-CH_2-O$; and 4) 79-82 ppm from -CH-O- as shown in Fig. 6 [20].

3. Results and Discussion

3.1 Etherification of glycerol

The etherification for the small scale (10 g) of etherification of glycerol with sodium carbonate by microwave irradiation in an open vessel mode CEM Discover® SP operating at 2.45 GHz and 300 W maximum power output is given in Fig. 3. The conversion (X) and the combined yield toward diglycerols, triglycerols, and tetraglycerols ($Y_{DG+TG+TtG}$) increased when the catalyst concentration increased from 1 wt% to 3 wt%. Moreover, the longer reaction time resulted in the higher conversion (X) and yield ($Y_{DG+TG+TtG}$). The higher temperature (270 °C) provided higher yields of the desired products than the lower temperature of 220 °C. However, at the higher temperature, cyclic diglycerols were observed, whereas the conditions with lower temperature did not generate cyclic diglycerols. The amount of cyclic diglycerols also increased with longer reaction times. Based on the criteria to achieve the highest conversion of glycerol, the highest $Y_{DG+TG+TtG}$, and the lowest S_{PG} and S_{c-DG}, the optimal conditions were obtained from the microwave reactor at 270 °C, microwave power of 300 W, in the presence of 1 wt% Na_2CO_3 catalyst at a reaction time of 1.5 h. In these conditions, the conversion, the combined yield ($Y_{DG+TG+TtG}$), the selectivity to pentaglycerols (S_{PG}), and the selectivity to cyclic diglycerols (S_{c-DG}) were 71, 68, 0, and 4 %, respectively.

3.2 Scale up of etherification reaction

In order to translate the technology obtained from the optimized etherification in a small scale toward an industrial scale, a process development of the reaction at a 1 kg scale was carried out. The first considerations were on the magnetron to generate microwaves. Due to the 100-fold increase in reaction scale and the cost of the magnetron, an alternative microwave radiation from a household microwave was used in this scale up experiment. The magnetron equipped in a household microwave represents an inexpensive and robust magnetron that showed the economical feasibility of the developing etherification process for a real industrial application. A magnetron with 1000 W capability was evaluated as the only heat source needed for a 1 kg scale of the glycerol etherification.

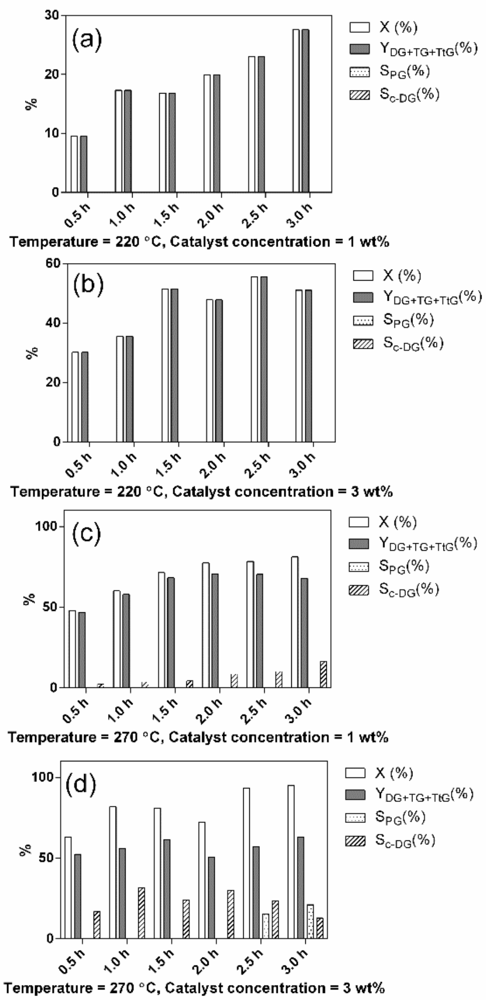

Fig.3. Results from etherification reactions of glycerol carried out in different conditions at a 10 g scale for the purpose of reaction optimization. The reaction temperature and catalyst concentration were the following: (a) 220 °C and 1 wt%; (b) 220 °C and 3 wt%; (c) 270 °C and 1 wt%; (d) 270 °C and 3 wt%. The reaction times were 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 h, and the maximum microwave power was 300 W. The conditions were compared to see the response of interests, including the conversion of glycerol (X), the combined yields of the desired products ($Y_{DG+TG+TtG}$), the selectivity toward pentaglycerols (S_{PG}), and the selectivity toward cyclic diglycerols (S_{c-DG}).

An important advantage of microwave radiation over conventional heating at the 1 kg scale reaction was experimentally addressed. It was found that at the 1 kg scale, it was difficult to rely on a conventional heat source with similar power to heat the reaction mixture to achieve a sufficient temperature for the polyglycerol products to form (220 °C - 270 °C). On the other hand, the much less expensive household microwave oven can provide sufficient heat for the majority of glycerol molecules to undergo etherification. Although the conventional household microwave oven has several limitations, it serves as a good microwave reactor at the 1 kg scale of glycerol etherification. This result illustrated the advantage of the precise and direct heating of microwave radiation over conventional heating.

For the experiments performed on a 10 g scale, it was found that when both reaction temperature and catalyst concentration were increased, the glycerol conversions were high, but at the same time, too much of the undesired cyclic diglycerols as well as pentaglycerols were formed. Therefore, a higher range of temperature and catalyst concentration should not be applied at the same time. To minimize the cost from the power consumption, in the 1 kg scale, 3 wt% of catalyst was used, while the reaction temperature was limited to ~ 230 °C. In addition, the higher concentration of the catalyst at a lower temperature provides higher combined yields of the desired products with only a small amount of the undesirable cyclic diglycerols, which can be removed by a vacuum distillation. The undesired products can also be generated at longer reaction times; therefore, the reaction time should not exceed 1.5 h.

At the 3 wt% catalyst concentration, a microwave power of at least 1000 W was found to be sufficient for the etherification to take place satisfactorily. One of the major costs of the industrial production is from the heating energy; therefore, the process development at 1 kg was performed with a minimum power of 1000 W.

The values of glycerol conversion (X), the combined yield ($Y_{DG+TG+TtG}$), the selectivity towards pentaglycerols (S_{PG}) and the selectivity towards cyclic diglycerols (S_{c-DG}) were determined. The experimental results are shown in Fig. 4.

At a 1 kg scale, it can be observed that at longer reaction times, the glycerol conversion as well as the combined yields ($Y_{DG+TG+TtG}$) increased. As expected, the longer reaction times of 85 min and 90 min led to more formation of larger polyglycerols (e.g. pentaglycerols). The generation of cyclic diglycerols in the 1 kg scale reactions is acceptable for all conducted experiments.

In an attempt to minimize the generation of pentaglycerols, we conducted and investigated a follow up experiment at a lower microwave power of 700 W (3 wt% Na_2CO_3, and reaction time of 3 h). The results of these milder reaction conditions gave better results concerning the formation of cyclic diglycerols and pentaglycerols. At the lower microwave power, the conversion of glycerol and the combined yield of polyglycerols are considerably lower at 51% and 50%, respectively. Only 1.39 % of cyclic diglycerols and no pentaglycerols were found.

The overall conversion of the investigated reactions was rather low for the reaction times of less than 85 min. Without further processing, only the results from the reaction run for 1.5 h met the specification set by the European Union (EU) that the total amount diglyerols, triglycerols, and tetraglycerols must be at least 70-75% in the mixture of polyglycerols to be used as food additives [16, 17]. A vacuum distillation was introduced at the end of the reaction to purify the crude mixtures.

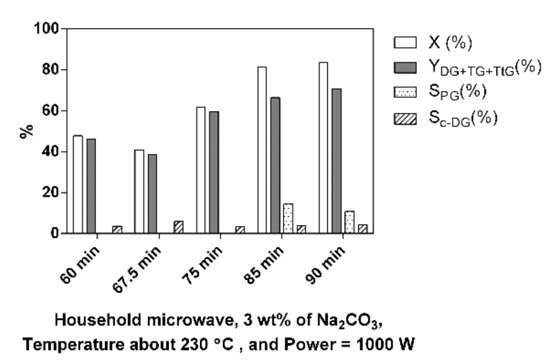

Fig.4. Results from etherification reactions of glycerol carried out at a 1 kg scale for the purpose of process development. The responses of interest include the conversion of glycerol (X), the combined yields of the desired products ($Y_{DG+TG+TtG}$), the selectivity toward pentaglycerols, and the selectivity toward cyclic diglycerols (S_{c-DG}), of a 1 kg scaling up of glycerol etherification toward polyglycerols at the reaction temperature of 230 °C, 3 wt% catalyst concentration, and at a microwave power of 1000 W.

3.3 Vacuum distillation process

After the vacuum distillation, the compositions of the desired polyglycerols were vastly improved. As shown in HPLC chromatograms in Fig. 5, the vacuum distillation removed most of the glycerol and cyclic diglycerols due their lower boiling points than other polyglycerols.

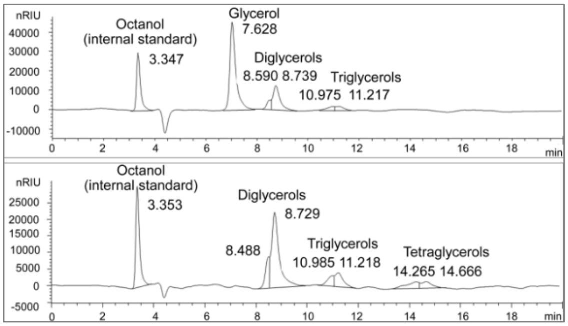

Fig.5. A comparison of refractive index HPLC chromatograms of (a) before and (b) after vacuum distillation of crude polyglycerol products (from etherification at 1 kg scale; 230 °C; 67.5 min and distillation of 100 g; 200 °C; 2.5 h).

All purified products showed significant increases in the composition of the desired products (92 %, 97 %, and 80 %, Table 1). The undesired cyclic diglycerols were efficiently removed by the vacuum distillation. Therefore, a sharp decrease in the content of the cyclic-diglycerols was observed. The results suggest that a vacuum distillation should be a part of the process because the left over glycerol and cyclic diglycerols can be efficiently separated from the crude products to increase the percent contents of the desired polyglycerols. Therefore, if the targets of the production are small polyglycerols such as diglycerols and triglycerols, the reaction conditions should be carried out at milder conditions to prevent the generation of the larger molecules of polyglycerols, which may not be removed by the vacuum distillation.

The best polyglycerol quality after vacuum distillation can be achieved in Entry 2 of Table 1. The conditions gave the most desirable polyglycerols. The combined content of diglycerols, triglycerols, and tetraglycerols yield was almost 98 %. Additionally, the amount of cyclic diglycerols in the product is less than 1.5 %. In general, the vacuum distillation is a promising purification process to improve the quality of the products obtained from the etherification of glycerol. The ^{13}C-NMR spectra of standard polyglycerols and polyglycerol products after distillation are almost identical to the spectrum of the mixture of the standard diglycerols, triglycerols, and tetraglycerols as shown in Fig. 6.

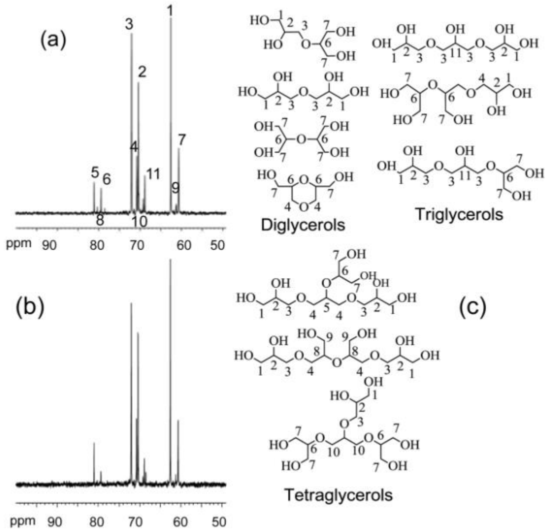

Fig.6. (a) ^{13}C-NMR spectrum of DG+TG+TtG standards, (b) ^{13}C-NMR spectrum of polyglycerol products after distillation (from etherification at 1000 W (Household MW); 200 °C; 67.5 min and distillation of 100 g; 200 °C; 2.5 h), and (c) the possible structures of polyglycerols and their isomers identified from the spectrum with NMR assignments.

Table1. Product compositions before and after 2.5 h vacuum distillation at 200 °C and high vacuum (ultimate pressure 2 x 10^{-3} mbar) of various reaction conditions by 3 wt% of Na_2CO_3.

Entry	Reaction conditions	% Compositions					
		DG+TG+TtG		PG		c-DG	
		Before	After	Before	After	Before	After
1	CEM microwave 25 W, 240 °C, and 60 min	60.09	92.62	0.00	0.00	3.32	1.77
2	Household MW 1000 W, 230 °C, and 67.5 min	38.47	97.70	0.00	0.00	5.90	1.43
3	Household MW 1000 W, 230 °C, and 90 min	70.65	79.80	10.77	18.89	4.20	0.57

4. Conclusion

In summary, the scale up process of etherification of glycerol to polyglycerols from 10 g scale to 1 kg scale has been successfully performed using microwave radiation. The reaction was scaled up to see the feasibility of microwave radiation for the etherification of glycerol on a larger scale (1 kg) by a less expensive and robust microwave magnetron in a household microwave oven. At a reaction temperature of 230 °C, microwave power of 1000 W, 3 wt% Na_2CO_3, and 1.5 h reaction time, we found that the conversion, the combined yield of diglycerols, triglycerols, and tetraglycerols, the selectivity to pentaglycerols, and the selectivity to cyclic diglycerols were 84, 71, 11, and 4 %, respectively. At longer reaction times, the glycerol conversion and combined yields of desired products increased. However, the increases in reaction time and temperature resulted in the formation of undesired cyclic diglycerols and larger polyglycerol molecules.

A vacuum distillation process was applied to improve the purity of the desired polyglycerols to a commercial grade level set by the EU. After the vacuum distillation under high vacuum (ultimate pressure 2 x 10^{-3} mbar) at 200 °C, the compositions of the desired polyglycerols (diglycerols, triglycerols, and tetraglycerols) were vastly improved to 98%. The vacuum distillation efficiently removed most of the glycerol and the undesired cyclic diglycerols, as verified through HPLC analyses, because of their lower boiling points. This study verifies the feasibility of the application of microwave radiation in etherification of glycerols to polyglycerols at 1 kg scale. The resulting polyglycerol mixture could be further purified by vacuum distillation to meet the standard requirement of commercial polyglycerols for food additives as set by the European Union.

5. Acknowledgements

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List of all symbols and abbreviations

DG – Diglycerols
TG – Triglycerols
TtG – Tetraglycerols
PG – Pentaglycerols
c-DG – Cyclic diglycerols
X – Glycerol conversion
$Y_{DG+TG+TtG}$ – Combined yields of diglycerols, triglycerols and tetraglycerols
$S_{c\text{-}DG}$ – Selectivity towards cyclic diglycerols
S_{PG} – Selectivity towards pentaglycerols
HPLC – High performance liquid chromatography
^{1}H-NMR – ^{1}H Nuclear magnetic resonance spectroscopy
^{13}C–NMR – ^{13}C Nuclear magnetic resonance spectroscopy
ESI-MS – Electrospray ionization mass spectrometry
IR thermometer – Infrared thermometer
JECFA – The Joint FAO/WHO Expert Committee on Food Additives
EU – The European Union