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Optimization of microwave-assisted etherification of glycerol to polyglycerols by sodium carbonate as catalyst

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HIGHLIGHTS

- Process optimizations on the etherification of glycerol to polyglycerols are reported.
- Reaction temperature is the most significant variable for the optimized process.
- Microwave radiation shortens the reaction time for the etherification of glycerol to oligoglycerols.
- HPLC was used to determine the quantity of polyglycerol products without any product modifications.

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ABSTRACT

The process optimization of etherification of glycerol to polyglycerols by sodium carbonate as a catalyst using microwaves as a heat source in solvent free conditions has been investigated in this study. The regression models describing the linear correlations between reaction parameters and reaction outcomes were developed. The three reaction parameters studied are: reaction temperature (220 °C and 270 °C), catalyst concentration (1 wt% and 3 wt%), and reaction time (0.5, 1.0, 1.5, 2.0, and 3.0 h). The reaction temperature was found to have the most significant effect on the percent conversion of glycerol (X); combined yields of diglycerols, triglycerols, and tetraglycerols products ($Y_{DG+TG+TtG}$); selectivity toward pentaglycerols (S_{PG}); and selectivity toward cyclic diglycerols ($S_{c\text{-}DG}$). Undesirable cyclic diglycerols formed at high temperature and the amount increased along with the longer reaction time. The higher catalyst concentration (3 wt%) provides higher amounts of the desired products. Moreover, the longer reaction time also resulted in higher conversions and yields. For the optimized conditions, X, $Y_{DG+TG+TtG}$, and $S_{c\text{-}DG}$ were predicted to be at 84%, 63%, and 9%, respectively, at the reaction temperature of 270 °C, catalyst concentration of 3 wt%, and reaction time of 1.0 h. Experimental verification of the predicted optimum conditions gave the actual responses of 93%, 70%, and 7% for X, $Y_{DG+TG+TtG}$, and $S_{c\text{-}DG}$, respectively, with small deviations from the predicted responses. The results indicated that the developed models were valid and accurate in describing the actual experimental data at any conditions within the range studied. The observation suggests that the sodium carbonate catalyst with microwave heat source have the potential to be used in glycerol conversions to polyglycerols.

1. Introduction

Biodiesel is a clean, renewable, and efficient alternative fuel to replace petroleum diesel which is predicted to be depleted in supply, and recently raises concerns on greenhouse gas concentrations [1]. Biodiesel can be produced by transesterification of animal or vegetable oils with alcohols, especially methanol. Glycerol is a main by-product from the transesterification process [2]. Glycerol supply exceeds its demand because of the recent dramatic growth of the biodiesel industry, resulting in the plunge of glycerol price [3]. Conversions of glycerol to other higher-valued chemicals are currently a focus of global research. Glycerol is a suitable starting material for a variety of chemical intermediates because of its nontoxic, edible, bio-sustainable, and biodegradable properties [4]. Cost-effective conversions of glycerol to valuable chemicals are necessary in order to improve the economy of the whole biodiesel

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production process [5,6]. Glycerol can be used as a reactant in oxidation processes, fermentation process, acetylation processes with acetic acid, and acetalization processes with ketones. Valuable chemicals obtained from glycerol include glyceraldehyde, dihydroxyacetone, hydroxyl pyruvic acid glycolic acid, and glyceric acid [7], 1,3-propanediol [8], polyglycerol esters [9,10], and oxygenated acetals and ketals [11–13]. Glycerol by-product from biodiesel production can be a source for the preparation of acidic catalysts for utilization in etherification reactions producing oxygenated additives for fuels [14]. Oxygenated components such as polyglycerols and polyglycerol ethers derived from etherification process are efficient chemical platforms [15]. Oligoglycerols, especially diglycerols and triglycerols (DG and TG, respectively) are of industrial interest because of their useful applications as components in cosmetics, polymers, food, and pharmaceutical industries [4]. Bigger oligoglycerol molecules such as pentaglycerols and the de-emulsifier cyclic diglycerols are not desired for food applications (JECFA [28,29]). The investigations of etherification of glycerol have been done by using both homogeneous and heterogeneous catalysts [16–21]. These studies were carried out by conventional heating which usually required longer reaction times. The current study reveals a key advantage of the heating by microwave radiation in shortening the reaction time required for the etherification.

Previously, several homogeneous catalysts such as Cs_2CO_3, NaOH, Na_2CO_3, CsOH, and H_2SO_4 have been examined for the conversion of glycerol to polyglycerols. Homogeneous catalysts provide higher glycerol conversions but lower selectivity to DG and TG, when compared with heterogeneous catalysts [21]. Alkali hydroxides are generally more active than carbonate bases due to the more basic strength of the hydroxide, but are less soluble in glycerol than carbonates [21].

During the etherification of glycerol, the electrophilic carbinol carbons are attacked by either primary or secondary hydroxyls in intermolecular or even intramolecular fashion. Polyglycerols are formed through consecutive etherifications where the glycerol molecules are condensed in linear, branched, or cyclic fashions [22]. In general, heterogeneous catalysts hold the advantages of the ease in separation and reusability but they give poorer activity when compared to homogeneous catalysts. Some heterogeneous catalysts cannot be employed in industry because of the difficulty in production and high cost. Other disadvantages of heterogeneous catalysts include leaching of chemicals, solubility in polar solvent, low thermal stability, and high reaction temperature and long reaction time requirements [16–18]. For heterogeneous catalysts, especially, mesoporous materials are applied because they can improve selectivity though its limited pore size to favor low molecular weight oligomers, which are DG and TG [23]. Many efforts have been made to control the selectivity towards small oligoglycerols by investigating the effect of heterogeneous catalysts, such as impregnated Cs-MCM-41, grafted Al_gSi-MCM-41, zeolite NaBeta, MgAl mixed oxides, and colloidal CaO [17,24,25]. Selectivity towards oligoglycerols tends to decrease at higher glycerol conversion because oligoglycerols are further converted into larger polyglycerols, in particular diglycerols and triglycerols are converted into larger polyglycerols. Reaction times required in most studies were longer than 24 h.

A study reported the application of microwave radiation as a heat source in the synthesis of polyglycerols from glycerol carbonate. It was found that the microwave radiation helps to improve the reaction yield and shorten the reaction time resulting in less energy consumption [26]. Only the polymerization of polymethylmethacrylate (PMMA), polymethylacrylate (PMA), and polystyrene (PS) at commercial scale applications were carried out by microwave heating [27].

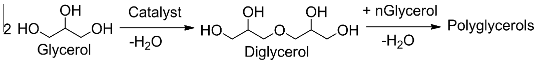

Fig. 1. Catalytic etherification of glycerol to polyglycerols.

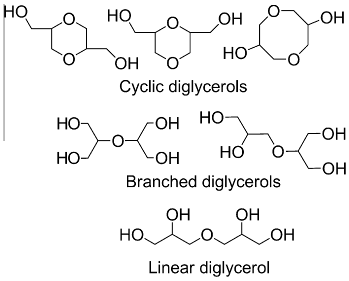

Fig. 2. Possible isomers of diglycerol products formed during etherification of glycerol [21].

This work aims to optimize the chemical conditions for the solvent-free microwave-assisted glycerol etherification by full factorial design at 2 levels to achieve the highest combined yields of small polyglycerols including diglycerols (DG), triglycerols (TG), and tetraglycerols (TtG). These three products can be used as additives in food applications. According to The Joint FAO/WHO Expert Committee on Food Additives (JECFA) specifications of polyglycerols composition, the polyglycerols in food additive can be the mixture of diglycerols, triglycerols, and tetraglycerols which must not be less than 70–75%, and there should not be more than 10% heptaglycerols (or bigger) in the composition [28,29].

In the present study, a sodium carbonate catalyst (Na_2CO_3) was the catalyst of choice because of its availability and high solubility in glycerol. Moreover, metal carbonate catalysts were chosen because: (i) base-catalyzed glycerol etherification pathway was reported to suppress the formation of undesirable cyclic oligomers and acrolein [23,30]; (ii) carbonates were found to be more active than hydroxides because of their higher solubility in glycerol [31]. Microwave radiation was utilized as the heat source in order to overcome the typical long reaction time for the etherification of glycerol. The key reaction parameters investigated in the optimization process were reaction temperature, reaction time, and catalyst concentration. The polymer products were purified by column chromatography and characterized by nuclear magnetic resonance (NMR) (both ^1H NMR, ^{13}C NMR), and electrospray ionization of high resolution mass spectrometry (ESI-HRMS). High performance liquid chromatography (HPLC) was used for qualitative and quantitative analyses. The etherification of glycerol and the possible products are shown in Figs. 1 and 2, respectively.

2. Materials and methods

2.1. Reaction procedure and product analysis

Specific amounts of Na_2CO_3 catalysts (Merck, Germany) were added to glycerol (10 mL) in a round bottom flask (100 mL). Glycerol etherification was conducted in a stirred microwave reactor, without additional solvent under various conditions as the followings: reaction temperatures of 220 °C and 270 °C, catalyst concentrations of 1 wt% and 3 wt%, microwave power of 25 W, atmospheric pressure, and reaction time of 0.5–3 h. Sample collections (0.1 mL) 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 the evaporated water from re-entering the system, a bump trap and a condenser (25 °C) were connected to the