Synthesis of Polyglycerol under Superbasic Conditions to Reduce the Severity of the Reaction Conditions

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Abstract. The increasing biodiesel production in Indonesia will affect the supply of glycerol because it is a by-product of the transesterification reaction. Abundant glycerol can provide added value if further processed into higher-value products such as polyglycerol. Polyglycerol is made from the polymerization of glycerol with the help of an alkaline catalyst, such as KOH, but the temperature and reaction time used are very high and long. Therefore, this study aims to increase the conversion of glycerol by adding DMSO to the glycerol and KOH solution to increase the basicity of the mixture, increase the polymerization rate, and decrease the temperature and reaction time. The conversion of glycerol to polyglycerol with the addition of 10 mL DMSO to the KOH and glycerol mixture, giving a DMSO to KOH-glycerol volume ratio of 1:5, with a reaction time of 2 hours and a reaction temperature of 140-150°C was 77%, compared to without the addition of KOH which required a reaction time of 8 hours and a reaction temperature of 260-280 °C resulting in a glycerol conversion of 99%. Adding DMSO, with constant KOH-glycerol volume, affects the polymerization reaction because compared to adding 5 mL DMSO (volume ratio of 1:10), the resulting glycerol conversion is 16%. For the effect of reaction time on the results of glycerol polymerization, 5 mL DMSO shows that the longer the time, the more polyglycerol formed can depolymerize into short-chain oligomers or back into glycerol. The optimum reaction time for 5 mL DMSO is 6 hours because the glycerol conversion is 63%, producing diglycerol and triglycerol with 30% and 17% selectivities, respectively.

Keywords: Diglycerol, DMSO, Glycerol, KOH, Polyglycerol

INTRODUCTION

Indonesia's dominance in global Crude Palm Oil (CPO) production peaked in 2023 with 50.07 million tons, representing a 59% share worldwide. This steady increase in CPO output fuels the expansion of various CPO-derived products, notably cooking oil and

biodiesel.

Biodiesel, also known as Fatty Acid Methyl Ester (FAME), is a renewable fuel produced through the esterification or transesterification of fatty acids found in vegetable oils like palm, sunflower, rapeseed, soybean, corn, and waste frying oil (Sumatri *et al.*, 2023). Indonesia's reliance on palm oil as its primary biodiesel feedstock has led to a surge in domestic biodiesel production, nearly doubling output from 6.17 million kiloliters in 2018 to 13.15 million kiloliters in 2023 (APROBI, 2024).

The biodiesel industry's reliance on transesterification results in a significant byproduct: crude glycerol. This mixture contains ash, catalyst, soap, free fatty acids, and glycerol, forming roughly 10% of the total biodiesel output (Chilakamarry *et al.*, 2021). Indonesia's 2023 biodiesel production implies the generation of 1.315 million kiloliters (1.157 million tons) of crude glycerol. Traditionally, this byproduct is purified for use in food, cosmetics, pharmaceuticals, and fuel industries (Sulistyo *et al.*, 2020). However, the expanding biodiesel industry could drive down glycerol prices, necessitating its utilization in higher-value products such as polyglycerol, 1,3-propanediol, and nitroglycerin (Chong *et al.*, 2020).

Polyglycerol is a synthetic organic compound formed by linking multiple glycerol molecules, as illustrated in Figure 1. The most common method for polyglycerol production is condensation polymerization of glycerol, which employs an alkaline catalyst and high temperatures due to the high activation energy required for the reaction to proceed. In Figure 1, the variable "n" represents the number of glycerol monomers linked together minus two. For instance, if three glycerol molecules are joined, the resulting compound is triglycerol, which consists of three glycerol units and an "n" value of one. This reaction also produces water as a byproduct, with two water molecules formed per reaction cycle, reflecting the constant reaction number of two.
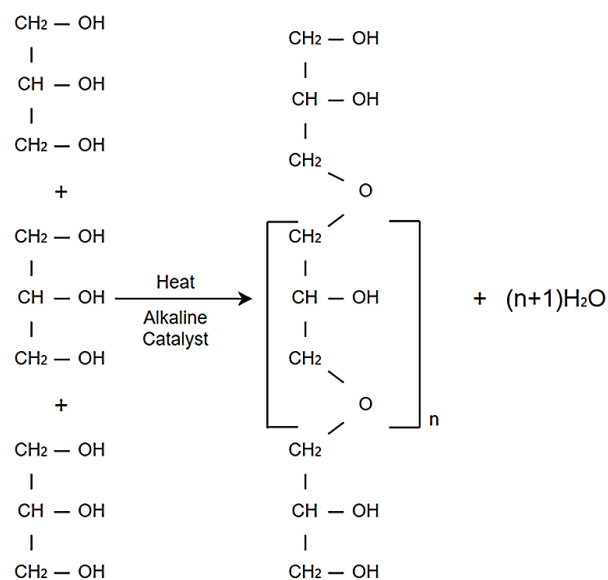

Fig. 1: Condensation Polymerization of Glycerol (Source: Babayan and Lehman, 1972)

It is important to note that polyglycerol is not a single, uniform compound but a diverse mixture of interconnected molecules with varying chain lengths and structural complexities, collectively called oligomers.

Recently, interest in polyglycerol has grown significantly, driven by its exceptional properties and potential applications. One key advantage of polyglycerol is its ability to serve as a foundation for numerous derivative compounds. By attaching different molecules, scientists can create materials with specific functionalities. For instance, polyglycerol polyricinoleate (PGPR, also known as E476) and polyglycerol esters of fatty acids (PGEs, or E475) are derived from

polyglycerol and find valuable applications in the food industry. These act as emulsifiers, ensuring a smooth and even distribution of ingredients, as described by Birk Lauridsen, (1976).

The benefits of polyglycerol extend beyond the food sector. When reacted with fatty acids, polyglycerol becomes a versatile ingredient in cosmetics. It offers several advantages, including preventing caking, improving skin feel, controlling viscosity, and, once again, acting as an emulsifier to create stable and well-blended cosmetic formulations.

Traditional polyglycerol synthesis relies on alkaline catalysts under elevated temperatures (220-260°C) and atmospheric pressure (Babayan and Lehman, 1972). However, the lengthy reaction time (8-24 hours) and high temperature pose challenges for economic large-scale production. Therefore, optimizing reaction conditions to improve efficiency and cost-effectiveness for industrial applications is crucial. Currently, the Epicerol® process dominates industrial polyglycerol production. This method involves reacting glycerol with hydrochloric acid using Lewis acid catalysts, followed by alkaline hydrolysis. However, its reliance on highly toxic and carcinogenic raw materials presents significant safety and environmental concerns, necessitating the exploration of alternative, sustainable methods (Ebadipour et al., 2020).

Understanding the factors influencing the polymerization rate is crucial for sustainable polyglycerol production. Garti et al., (1981) investigated the influence of various catalysts on polyglycerol synthesis under an inert atmosphere at 260°C. Their findings revealed that K_2CO_3 exhibited the highest catalytic activity, followed by Li_2CO_3, Na_2CO_3, and hydroxides, despite the stronger basicity of hydroxides. This was attributed to the higher solubility of carbonates compared to hydroxides. They further studied the effects of temperature and catalyst loading at a 4-hour reaction time using 2.5 mol% NaOH. Increasing the temperature from 240°C to 260°C led to a significant increase in water yield (7.5 to 14 mL per mole glycerol), indicating higher oligomer production. However, a further rise to 270°C and 280°C resulted in shorter reaction times (2.5 and 1 hour, respectively) but did not significantly increase water yield (15.8 and 16.2 mL per mole glycerol). Similarly, increasing catalyst loading mirrored the effect of temperature. The key findings from this study highlight that the polymerization rate is collectively influenced by the catalyst's solubility and basicity, reaction temperature, catalyst concentration, and reaction time.

Building upon the work of Garti et al., (1981), this study investigates the potential of using a potassium hydroxide (KOH)/ Dimethyl Sulfoxide (DMSO) mixture as a catalyst for glycerol polymerization. Garti et al. observed that increasing catalyst basicity could increase the polymerization rate. We propose that combining KOH, a strong base, with DMSO could create a stronger basic medium, which has a high pKa (30-32) according to the research conducted by (Yuan et al., 2010), potentially achieving the desired effects. To our knowledge, prior research has yet to explore using KOH/DMSO for glycerol polymerization. This study employs a comparative approach to evaluate a novel catalyst's effectiveness, measuring reaction yield and efficiency under varying conditions: KOH/DMSO vs. KOH alone, with adjustments to DMSO volume and reaction time.

RESEARCH METHODOLOGY

Materials

Both glycerol (99% purity) and KOH were purchased from ROFA Laboratorium Center, while analytical grade DMSO was obtained from Merck Millipore. All chemicals were utilized as received without any prior purification or pre-treatment. The reaction was conducted using a constant 50 mL volume of the KOH-glycerol mixture, with 5 mL and 10 mL of DMSO, corresponding to volume ratios of 1:10 and 1:5, respectively, for DMSO to the KOH-glycerol mixture.
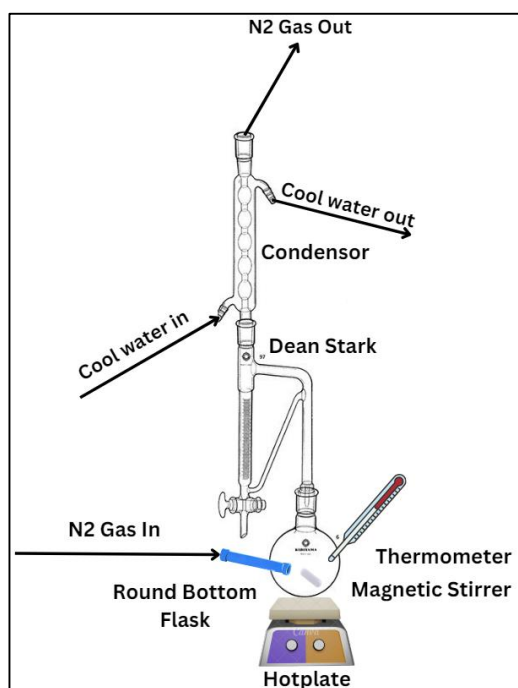

Fig. 2: Schematic diagram of the reaction apparatus for glycerol polymerization

Polymerization Reaction

The polymerization reaction was conducted using a standard setup consisting of a Dean-Stark trap, condenser, hot plate, magnetic stirrer, Erlenmeyer flask, hoses, and a gas washing bottle (Figure 2). The Dean-Stark trap separated the water byproduct formed during the reaction, aided by the reflux condenser. A magnetic stirrer efficiently mixed the reaction components: KOH, glycerol, and DMSO. The gas washing bottle, filled with an appropriate desiccant, prevented air ingress and allowed the safe release of nitrogen gas to maintain an inert atmosphere.

Sample Analyses

Polyglycerol analysis was performed using Waters™ high-performance liquid chromatography (HPLC) equipped with a Shodex™ SUGAR SH1011 column (8.0 mm I.D. x 300 mm). The mobile phase consisted of 2.5 mM H_2SO_4 aqueous solution, eluted at a flow rate of 0.6 mL/minute with a column temperature of 50°C.

Qualitative Analysis

Qualitative HPLC analysis of the research sample can be performed by comparing its chromatogram with standard glycerol and commercial polyglycerol. The standard glycerol chromatogram (Figure 3) peaks at approximately 15.361 minutes, corresponding to pure glycerol (99%). The commercial polyglycerol chromatogram (Figure 4) exhibits peaks at approximately 18.23, 16.70, 15.45, 14.44, 13.62, and 12.96 minutes, which can be used to identify glycerol, diglycerol, triglycerol, tetraglycerol, pentaglycerol, and hexaglycerol, respectively.
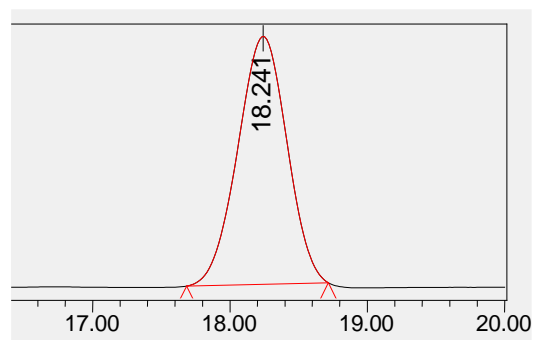

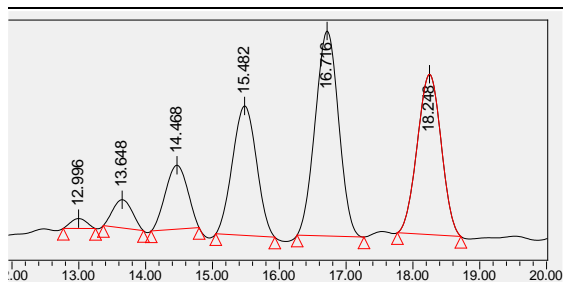**Fig. 3**: HPLC chromatogram of glycerol standard, prior to the maintenance

Fig. 4: HPLC chromatogram of commercial polyglycerol, prior to the maintenance

It is important to note that even slight variations in the sample analysis method can result in noticeable shifts in the peaks. Analyzing commercial glycerol and commercial polyglycerol alongside the tested samples is strongly recommended to ensure proper standardization of oligomer peaks, enabling more accurate and reliable identification of the compounds present. The author observed this phenomenon when the HPLC system underwent maintenance, leading to a noticeable shift in the oligomer peaks. For instance, the glycerol peak, typically observed at 18.241 minutes, shifted to approximately 15.376 minutes (Figure 5). Similarly, the peaks corresponding to other oligomers were also displaced, as demonstrated in the HPLC analysis of commercial polyglycerol (Figure 6). Although the peaks have shifted, they now match those shown on the official Shodex HPLC website (Figure 7). This suggests that the initial analysis, prior to the maintenance, was the one that deviated.
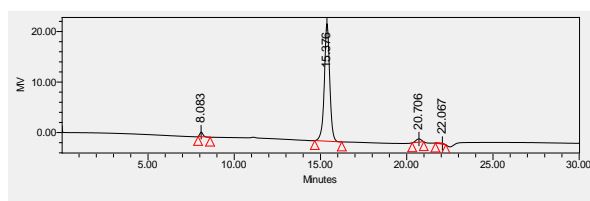

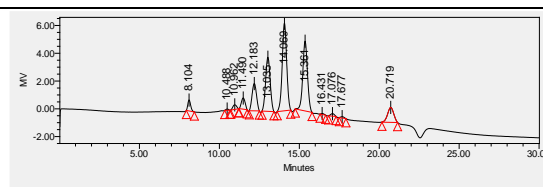**Fig. 5**: HPLC chromatogram of glycerol standard, following maintenance procedures.

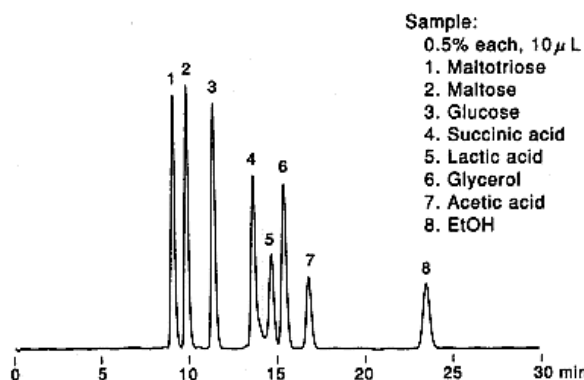**Fig. 6**: HPLC chromatogram of commercial polyglycerol, following maintenance procedures.

Fig. 7: Saccharides and organic acids (SH1011) (Source: Shodexhplc.com)

Table 1 shows the before and after peaks of the oligomers.

Table 1: The retention times of the peaks shown in the HPLC analysis

Compound	*Peak* (Before maintenance)	*Peak* (After maintenance)
Glycerol	18.248	15.361
Diglycerol	16.716	14.069
Triglycerol	15.482	13.035
Tetraglycerol	14.648	12.183
Pentaglycerol	13.648	11.490
Hexaglycerol	12.996	10.962

Quantitative Analysis

Due to the unavailability of pure oligomer standards, an alternative quantitative analysis approach was adopted. First, a standard curve was generated using pure glycerol to determine the total glycerol content in the sample. Then, the peak area of each oligomer was compared to the glycerol peak area, and

the mass of each oligomer was calculated by multiplying this ratio by the total glycerol mass. This approach enabled the estimation of each oligomer's mass and its subsequent selectivity determination, effectively using the available glycerol standard.

Fig. 8a: Glycerol with 99% purity
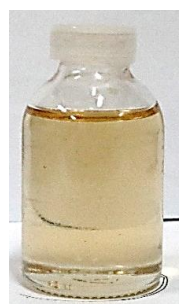

Fig. 8b: Commercial polyglycerol

Fig. 8c: Polyglycerol obtained after an 8-hour reaction at 220-230°C with KOH catalyst

Fig. 8d: Polyglycerol obtained after an 8-hour reaction at 260-270°C with KOH catalyst

RESULTS AND DISCUSSION

Catalytic Performance of KOH

The catalytic performance was evaluated using 2 mol% KOH. A constant 50 mL volume of the KOH-glycerol mixture was used. Table 1 shows that KOH alone achieved the highest glycerol conversion, likely due to the higher temperature and longer reaction time. This process produced polyglycerol with a 97.56% selectivity towards larger oligomers. HPLC analysis confirms the presence of abundant larger oligomers (peak at 8.397 minutes), with the glycerol peak at 17.826 minutes. Lower reaction temperatures (220°C and especially 140°C) resulted in significantly lower conversions, as expected based on Garti *et al.*'s findings (1981) that report minimal conversion at temperatures below 220°C.

No polyglycerol was formed when using KOH as a catalyst at a reaction temperature of 140–150°C and an 8-hour reaction time. This result can be attributed to the high activation energy required to initiate glycerol polymerization. At a higher temperature of 220–230°C and the same reaction time, glycerol polymerization commenced but progressed at a slower rate compared to the reaction at 260–270°C, where the polymerization process was significantly more efficient.

Figures 9, 10, and 11 depict the HPLC analysis of polyglycerol samples obtained after an 8-hour reaction time at various reaction temperatures (140–150°C, 220–230°C, and 260–270°C) using KOH as the catalyst without DMSO addition. As shown in Figure 9, only a single peak corresponding to glycerol is observed at a retention time of 15.205 minutes, indicating the absence of polyglycerol formation at 140–150°C. In contrast, Figure 10 reveals two additional peaks at 13.938 and 12.921 minutes, suggesting the formation of diglycerol and triglycerol at 220–230°C. Finally, Figure 11 shows a dominant peak at 9.875 minutes, indicating the presence of long-chain polyglycerol at 260–270°C. This peak is identified as long-chain polyglycerol because it cannot be conclusively associated with the peaks corresponding to diglycerol, triglycerol, tetraglycerol, pentaglycerol, or other shorter-chain oligomers observed in Figure 4. This suggests the formation of a more complex polyglycerol structure.
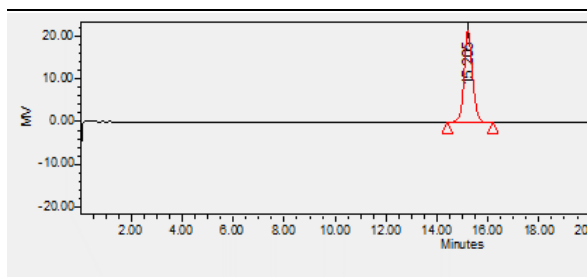
Fig. 9: HPLC analysis of the polyglycerol sample obtained after an 8-hour reaction at 140-150°C using KOH as the catalyst, without the addition of DMSO
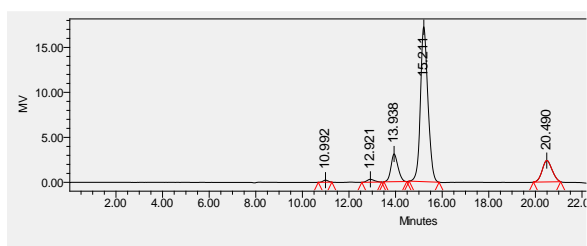

Fig. 10: HPLC analysis of the polyglycerol sample obtained after an 8-hour reaction at 220-230°C using KOH as the catalyst, without the addition of DMSO.
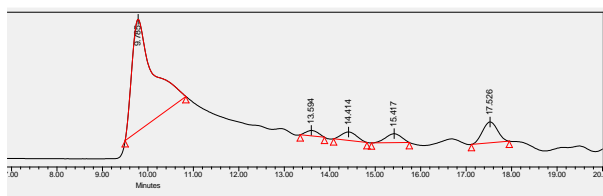

Fig. 11: HPLC analysis of the polyglycerol sample obtained after an 8-hour reaction at 260-270°C using KOH as the catalyst, without the addition of DMSO.

Catalytic Performance of KOH/DMSO Mixture

The catalytic performance was evaluated using 2 mol% KOH. A constant 50 mL volume of the KOH-glycerol mixture was used, with 5 mL and 10 mL of DMSO, corresponding to volume ratios of 1:10 and 1:5, respectively, of DMSO to the KOH-glycerol mixture.

The HPLC analysis of the polyglycerol sample with the addition of DMSO shows a peak at approximately 9.68 minutes. Based on the sequence of oligomers observed from the commercial polyglycerol chromatogram, this peak is assumed to be long-chain polyglycerol.

The addition of DMSO facilitated polymerization at lower temperatures (140-150°C, limited by DMSO's boiling point). This process resulted in a polyglycerol product with a significantly higher selectivity for diglycerol (Table 2 and Table 3). When using 5 mL of DMSO, diglycerol selectivity increased with reaction time, while the formation of larger oligomers (triglycerol, tetraglycerol, etc.) decreased after 6 hours (Figure 12). In contrast, with 10 mL of DMSO, the reaction rate significantly increased, achieving 71% conversion within 2 hours. However, the product selectivity shifted towards longer chains, with a higher proportion of tetraglycerol and larger oligomers than 5 mL DMSO. These observations highlight the influence of DMSO volume on reaction rate and product selectivity and suggest that extended reaction times with 5 mL DMSO do not favor the formation of longer oligomers. Instead, some polyglycerol may undergo depolymerization to shorter chains or even revert to glycerol (oxidation).

The glycerol converted from the 10 mL DMSO addition with 2 hours reaction time is much higher than the 5 mL DMSO addition, but the selectivity towards diglycerol and triglycerol is much lower. This result is caused by the faster polymerization rate of polyglycerol than the 5 mL DMSO addition, which caused the formation of many higher degrees of polyglycerol. The concept of solvation can explain the rapid increase in polymerization rate at lower temperatures after adding DMSO. Imagine OH- ions surrounded by glycerol molecules as tiny shields. These tiny shields would make it hard for OH- ions to interact with other molecules.

When DMSO is added, a solvent like DMSO that doesn't hold onto OH- ions as tightly as glycerol will disrupt the tiny shields. This frees up the OH- ions and makes them much more reactive (basic). DMSO can form strong bonds with glycerol molecules, reducing the tiny shields available for OH- ions. This bonding is like a handshake that keeps glycerol molecules busy. The addition of DMSO significantly increases the availability of free hydroxide ions (OH-) (Dolman and Stewart, 1966). These OH- ions then react with glycerol through condensation polymerization, forming polyglycerol (the main product) and water (the side product).

Increasing the reaction time to 4 hours with 10 mL DMSO resulted in a solid, polymerized product that was difficult to remove from the flask. As this is not the desired outcome for the target application in the food or cosmetic industries (which requires a liquid product), the 4-hour data should be included in Table 2.

Interestingly, the products obtained from 2-, 4-, 6-, and 8-hour reaction times with 5 mL DMSO (not shown) exhibited similar appearances to the 2-hour reaction product with 10 mL DMSO.
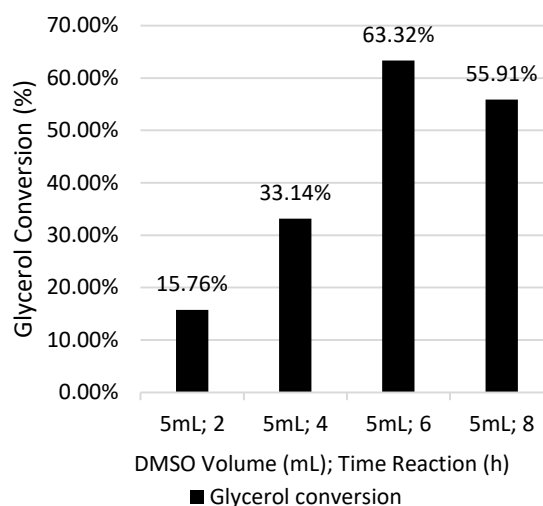

Fig. 12: Glycerol conversion at 2 mol% KOH with DMSO addition (5 mL) at various reaction times

Table 2: Glycerol conversion and polyglycerol selectivity with 2 mol% KOH, without DMSO addition, at various reaction times

DMSO Volume	$T_{reaction}$	$t_{reaction}$	Glycerol Conversion	PG2 Selectivity	PG3 Selectivity	PG4+ Selectivity	Unknown
mL	°C	h	%	%	%	%	%
0	140-150	8	0.00%	0.00%	0.00%	0.00%	0.00%
0	220-230	8	23.12%	6.80%	0.53%	3.58%	12.22%
0	260-270	8	98.80%	0.23%	1.01%	97.56%	0.00%

Table 3: Glycerol conversion and polyglycerol selectivity with 2 mol% KOH, with DMSO Addition, at various reaction times and DMSO volume

DMSO Volume	$T_{reaction}$	$t_{reaction}$	Glycerol Conversion	PG2 Selectivity	PG3 Selectivity	PG4+ Selectivity	Unknown
mL	°C	h	%	%	%	%	%
5	140-150	2	15.76%	9.57%	0.00%	6.19%	0.00%
5	140-150	4	33.14%	24.01%	6.50%	2.64%	0.00%
5	140-150	6	63.32%	29.91%	17.38%	12.71%	3.33%
5	140-150	8	55.91%	31.36%	14.97%	7.54%	2.03%
10	140-150	2	71.43%	22.99%	12.65%	32.93%	2.85%

Both samples, with (Figures 13a & 13b) and without DMSO (Figures 8c & 8d), exhibited a dark black color and strong odor. Previous research shows that the high reaction temperature likely contributes to the black color observed in samples without DMSO. Shaari *et al.* (2013) reported black polyglycerol formation at 250-270°C (US8404904B2), and Barros *et al.* (2017) observed a similar trend of darker colors with increasing temperature. High temperatures can promote charring, explaining the black color and potentially leading to glycerol/polyglycerol decomposition and acrolein formation (Garti *et al.*, 1981). Furthermore, the formation of long-chain polyglycerol might also contribute, as suggested by the black color produced when DMSO is added at low reaction temperatures. However, Kirby *et al.* (2015) suggest that undesired products, such as cyclic dimers, acrolein, and other dehydration products, could primarily cause a dark color.

Fig. 13a: Polyglycerol obtained after a 2-hour reaction with KOH catalyst and 10 mL DMSO addition

Fig. 13b: Polyglycerol obtained after a 4-hour reaction with KOH catalyst and 10 mL DMSO addition

Based on the HPLC analysis, a two-hour reaction time resulted in the formation of diglycerol, as indicated by a peak at 16.698

minutes in Figure 14. Traces of long-chain polyglycerol were also detected at 9.678 minutes. In contrast, Figures 15, 16, and 17 exhibit "backward" peaks, where the signal decreases rather than increases. This anomaly is likely due to a software error in the HPLC system. Figures 16, 17, and 18 correspond to reactions with 5 mL DMSO and an 8-hour reaction time and 10 mL DMSO and a 2-hour reaction time, respectively, peaking around 19.100 minutes. This peak is classified as unknown as it does not match any known compounds in the Shodex database or other literature. Given the reaction conditions and the common glycerol polymerization products, this peak may correspond to glycidol or acrolein, typical by-products of the polymerization process.
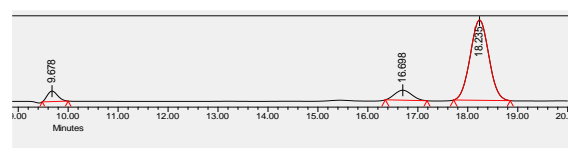

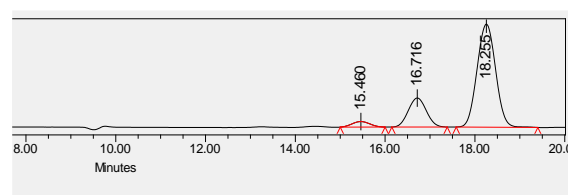**Fig. 14:** HPLC analysis of the experimental sample using KOH catalyst and 5 mL DMSO, reaction time = 2 hours

Fig. 15: HPLC analysis of the experimental sample using KOH catalyst and 5 mL DMSO, reaction time = 4 hours
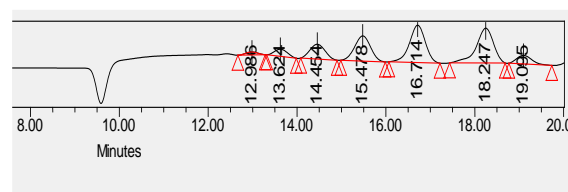

Fig. 16: HPLC analysis of the experimental sample using KOH catalyst and 5 mL DMSO, reaction time = 6 hours
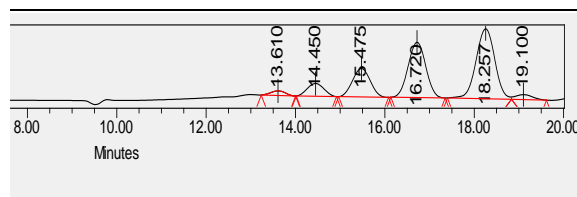
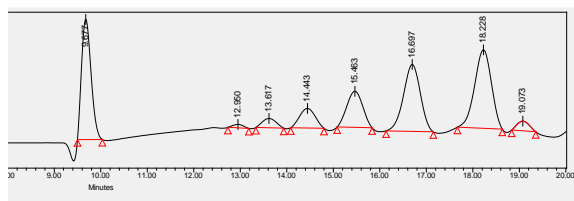**Fig. 17:** HPLC analysis of the experimental sample using KOH catalyst and 5 mL DMSO, reaction time = 8 hours

Fig. 18: HPLC analysis of the experimental sample using KOH catalyst and 10 mL DMSO, reaction time = 2 hours

Kinetic Analysis of Glycerol Conversion to Polyglycerol

Developing a simple kinetic model to determine the glycerol polymerization rate to predict glycerol conversion using DMSO in future experiments was essential. The most applied models for reaction kinetics are first-order and second-order reactions. In first-order kinetics, the reaction rate is directly proportional to the concentration of a single reactant, as demonstrated in Reaction 1 (R1). Conversely, in second-order kinetics, the reaction rate is proportional to the square of the reactant's concentration, as observed in Reaction 2 (R2).

$$r = k[A] \qquad \text{(R1)}$$
$$r = k[A]^2 \qquad \text{(R2)}$$

[A] represents glycerol, as outlined in the following chemical reaction:

$$Glycerol \xrightarrow{catalyst} Polyglycerol + H_2O$$

The integrated form of first-order law is represented in R3, whereas the integrated second-order law is represented in R4.

$$\ln\left(\frac{[A]_o}{[A]}\right) = kt \qquad \text{(R3)}$$

$$\frac{1}{[A]} = \frac{1}{[A]_o} + kt \qquad \text{(R4)}$$

For a first-order reaction, plotting $\ln\left(\frac{[A]_o}{[A]}\right)$ against time should give a straight line. It should yield a straight line. For a second-order reaction, plotting $\frac{1}{[A]}$ against time should produce a straight line. The reaction order can be determined by identifying the best linear fit model. This can be achieved by performing linear regression in Excel and comparing the R^2 values for each plot. First-order and second-order plots against time are as follows.

Both charts (Figures 19 and 20) exhibit a straight line from the 2-hour to the 6-hour mark, followed by a noticeable drop between 6 and 8 hours. By focusing on the linear trend observed from 2 to 6 hours, the first-order plot demonstrates a better fit with an R^2 value of 0,9383, as represented by the equation in R5. In comparison, the second-order plot for the same time range yields an R^2 value of 0,8932, with its corresponding equation shown in R6.
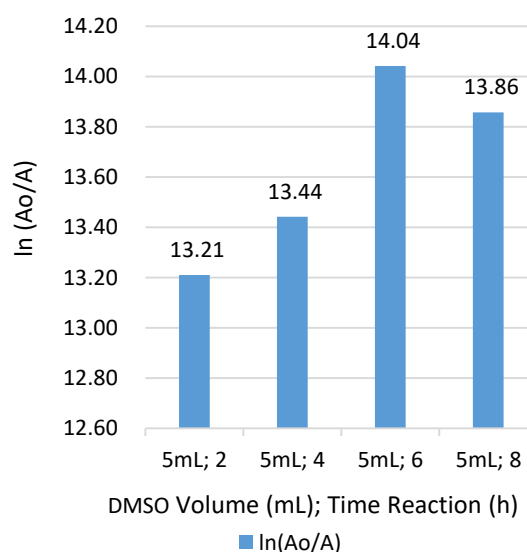

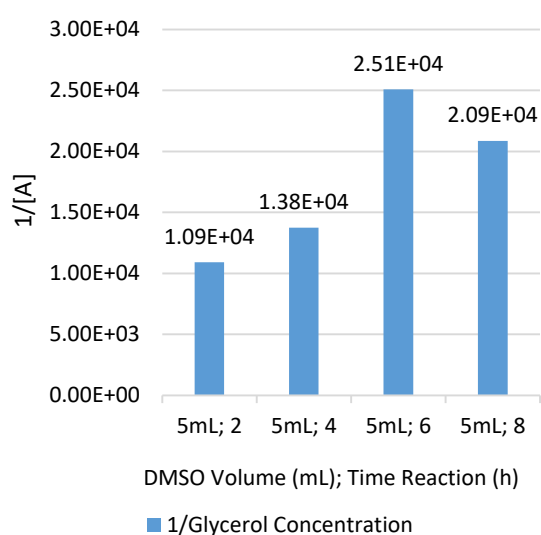**Fig. 19:** First-order plot against time

Fig. 20: Second-order plot against time

$$y = 0{,}4157x + 12{,}733 \quad \textbf{(R5)}$$
$$y = 7080x + 2427{,}4 \quad \textbf{(R6)}$$

The noticeable drop observed between 6 and 8 hours can be attributed to the depolymerization of polyglycerol into shorter oligomers or back into glycerol, as well as the potential occurrence of side reactions. This behavior is evident from the glycerol conversion data.

CONCLUSIONS

Our investigation demonstrates that DMSO significantly enhances the polymerization rate of glycerol using KOH catalysis, enabling polyglycerol production at milder temperatures and shorter reaction times. While high-temperature reactions without DMSO yield long-chain polyglycerol with near-complete glycerol conversion, adding DMSO offers advantages. With 10 mL DMSO, we achieved 77% glycerol conversion with 23% selectivity towards diglycerol and 33% towards long-chain polyglycerol in just 2 hours.

Exploring 5 mL of DMSO revealed a time-dependent effect. The optimal reaction time was 6 hours, yielding 63% glycerol conversion with high selectivity towards diglycerol and triglycerol. Further reaction time led to polyglycerol depolymerization into short-chain oligomers and glycerol. Notably, HPLC analysis revealed the presence of unidentified compounds at 19 minutes, indicating the need for further purification in downstream processing.

A simple kinetic analysis of glycerol conversion into polyglycerol indicates that the reaction follows first-order kinetics, as determined by the higher R^2 value compared to second-order kinetics. However, this observation only applies to the reaction with a DMSO-to-KOH-glycerol mixture ratio of 1:10 and a reaction time of less than 6 hours, as extended durations lead to the degradation of the main product.

ACKNOWLEDGEMENTS

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