

A PROCESS FOR PREPARING POLYMERS OF POLYHYDRIC ALCOHOLS

5 The present invention relates to a process for accelerating the conversion of linear polymers of polyhydric alcohols from their monomers in the presence of catalysts using microwave irradiation.

10 BACKGROUND ART

The present invention relates to the process of the production of polyhydric alcohols from their monomers. Examples of monomers that could be subjected to this process are glycerol, ethylene glycol, propylene glycol, sorbitol, sucrose, D-glucose and fructose.
15 This list is by no means exhaustive. Polyglycerol is defined as a polymer containing two or more units of glycerol and it may be either linear or branched.

Numerous methods are known for the preparation of polyglycerols with earlier works evolved around the use of thermal dehydration of glycerol. The polymerisation was
20 carried out at atmospheric pressure and at an elevated temperature, which is about 270°C - 280°C as mentioned in U.S. Pat No. 2,487,208. The process can be accomplished without the use of catalyst but the yield of polyglycerol is considerably low as reported by Hauschild and Petit (1956). Therefore, various catalysts have been introduced to aid in the formation of polyglycerol such as mixtures of sulphuric acid and triacetin as
25 described in U.S. Pat. No. 3,968,169, hypophosphorus acid with sodium hydroxide as appeared in US Pat. NO. 4,551,561, alkaline carbonates such as potassium carbonate with aluminium oxide as in J.P. No. 61,238,749 and sodium or potassium hydroxide as in U.S. Pat.No.5,710,350.

30 Polyglycerol formation was also reported with either solketal, glycidol or glycerol carbonate as the reactants when reacted with hydrotalcite at elevated temperatures as described in W.O. Pat. No.9,516,723. Other than that, rubidium, caesium and potassium fluoride salts on alumina or zeolites were used as catalyst for the polymerisation of

glycerol. In addition, glycidol, glycerol carbonate and solketal were polymerised using the above fluoride salts into polyglycerol as reported in W.O.Pat. No. 9,521,210. Other than that, in U.S. Pat No. 5,635,588, both linear and cyclic polyglycerols were products of reaction between glycidol, glycerol carbonate and solketal with beta-zeolites as
5 catalysts.

While some other literatures reported the use of epichlorohydrin in the process to prepare polyglycerol, in U.S. Pat. No. 4,960,953, Jakobson et al. disclosed a process to produce polyglycerol, which comprised reacting glycerol, diglycerol or higher polyglycerol with
10 epichlorohydrin at 90°C to 170°C to produce a crude chlorohydrin/ether mixture, followed by adding an amount of strong base at least substantially equivalent to the organically bound chlorine content of the chlorohydrin/ether mixture, and desalting the mixture and recovering the glycerol, diglycerol and higher polyglycerol fractions.

15 Allyl alcohol is another route in preparing polyglycerols. The process involve depoxidation of the allyl alcohol, in which glycidol would be formed and then followed by polymerisation of the glycidol. This was proven as another effective method to prepare polyglycerol as shown in J.P. No. 2,169,535.

20 Despite the fact that the background art in preparing polyglycerol is crowded and diverse, it is evident that the synthesis of polyglycerol and diglycerol from glycerol has one major drawback, which is the duration of reaction. It is a usual practice to have a reaction time of minimum 5 hours to 72 hours to carry out polymerisation with a mixed yield of glycerol, diglycerol, triglycerol and other higher polyglycerols. Other preparation such as
25 those that involve epichlorohydrin may polymerise at a faster rate, but polyglycerols produced from epichlorohydrin are not particularly favoured by the industry, as there may still be organically bound chlorine in the polyglycerols.

30 SUMMARY OF THE INVENTION

Prior art for the preparation of diglycerols and higher polyglycerols suffer from low yields and/or very long reaction times. This invention provides a process to reduce the

reaction time required for the production of diglycerol and higher polyglycerols. This is achieved by subjecting glycerol to the irradiation of microwave, which acts as a heat element for the polymerisation reaction. Microwave irradiation is proven to have accelerated the reaction greatly, in which the reaction time may be reduced to minutes.

- 5 This new approach was coupled with the use of specific catalysts for the formation of linear diglycerol and higher polyglycerols from glycerol.

In the present invention, glycerol is exposed to microwave irradiation for a certain period of time in the presence of a specific catalyst. Prolonged heating is to be avoided, as it will
10 favour the formation of high degree polyglycerols such as heptaglycerol, which is not favourable. Therefore, the duration and/or strength of the microwave irradiation are critical in determining the composition of the end products.

The specific catalysts used in the process are chosen to give significantly high conversion
15 percentage of glycerol to its polymers which are preferably, only linear diglycerol and higher polyglycerols. In this invention, high temperatures are employed to drive the conversion of glycerol to diglycerol and polyglycerols as milder temperatures tend to give poor yields of diglycerol and polyglycerols. However, colouration of the end products will result if the reaction temperature employed is too high. Therefore, an optimal range
20 of reaction temperature is chosen to produce high yields of diglycerol and polyglycerols of a good quality.

After the specific required reaction time, the end product obtained from the process is subjected to filtration to remove the catalyst. Further removal of the catalyst may be
25 achieved by subjecting an aqueous solution of the end product through an ion exchange column. The crude end product mixture is then dried from water by means of distillation. The dried crude end product is sent for HPLC analysis and based on the HPLC chromatogram; the composition of the crude end product may comprise of unreacted glycerol, diglycerol, triglycerol, tetraglycerol, pentaglycerol and hexaglycerol.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a significantly expedited process when compared with
5 conventional processes for the preparation of diglycerol and polyglycerols from glycerol.
The reaction time taken to produce diglycerol and polyglycerols, is reduced to about 20 to
30 minutes whereas the conventional methods may take about 5 hours to 72 hours. This
reduction in the conversion time is as a result of the use of microwave irradiation, in
which the glycerol is heated in a 900W microwave oven in the presence of a specific
10 catalyst and stirred with the aid from a magnetic stirrer.

It has been reported that polymerisation of glycerol to form polyglycerols can be carried
out without the use of catalyst but the reaction suffered low yield of polyglycerols.
Therefore, in this invention, a catalyst is selected to increase the yield of the desired
15 polyglycerols. It is found out that organic acid salts of alkaline metals gave good yields
and selectivity in producing diglycerol and polyglycerols from glycerol. Examples of
catalysts employed in the reaction are potassium acetate, sodium acetate anhydrous,
sodium acetate trihydrate, sodium formate, tri-sodium citrate and potassium citrate. In the
process, about 0.5 to 10 wt percent and, more preferably 0.5 to 1.0 percent of catalysts are
20 employed based on the weight of glycerol.

For this invention, the temperature may be in the range of 200°C to 310°C, but preferably
in the range of 250°C to 270°C. By employing temperatures in this range, it is possible
to achieve good conversion with minimal undesired side products while still obtaining
25 acceptable reaction rates. It is preferred that the process is conducted at atmospheric
pressure and therefore the use of costly high-pressure equipment is avoided.

The yield of crude end products, which will typically comprise of unreacted glycerol and
between 78% - 85% of diglycerol and polyglycerols by weight of the glycerol. The yield
30 of individual glycerol polymers and the selectivity of the reaction can be ascertained by
analysing the crude end product of the products using High Performance Liquid
Chromatography (HPLC). The conversion percentage of glycerol to polyglycerol
typically ranges from 75% -85%, with about 15%-20% of unreacted glycerol. The

following is a typical composition percentage of the glycerol polymers analysed through HPLC.

Typical composition of glycerol polymers:

- 15%-20% of unreacted glycerol
- 5 □ 25%-30% of diglycerol
- 20%-25% of triglycerol
- 10%-15% of tetraglycerol
- 15%-10% of pentaglycerol
- 1%-5% of hexaglycerol

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From the HPLC chromatogram, there is little or no evidence of cyclic diglycerol or polyglycerols found in the crude end product when compared to standard polymers of glycerol. Therefore, the process selectively produces linear diglycerol and polyglycerols from glycerol.

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The crude end product may be diluted with an equal amount of deionised water and is then subjected through a column of cationic ion exchanger such as Amberlite IR-120 to remove dissolved catalysts. The crude end product is then subjected distillation to remove the water added earlier.

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The following examples illustrate the process of the invention but are limitative thereof.

Example 1

- 25 Glycerol (50g) was charged into a 250ml round bottom flask and then into the same flask was added 0.5g of potassium acetate. The mixture was stirred for a minute with a magnetic stirrer in the 900W microwave oven cavity in order to homogenise the mixture. Then, the microwave oven was programmed to raise the temperature from ambient to 270°C in 2 minutes and this temperature was maintained for another 15 minutes, after
- 30 which the cooling process was started to mark the end of reaction. The total reaction time was just mere 17 minutes. After the end product was cooled, an equal amount of deionised water was added to the end product in order to dilute the viscous product. The diluted product was then subjected through an ion exchange column to remove dissolved

catalysts. The treated end product was later subjected to distillation to remove water. The treated end product was then subjected to High Performance Liquid Chromatography (HPLC) and the compositions of each polymers of glycerol were as below. The treated polyglycerols yield was 81% and the conversion percentage of glycerol to polyglycerol was 80%.

Typical composition of glycerol polymers for reaction product of Example 1:

- ☐ 19.6% of unreacted glycerol
- ☐ 25.4% of diglycerol
- ☐ 22.0% of triglycerol
- ☐ 15.6% of tetraglycerol
- ☐ 10.5% of pentaglycerol
- ☐ 6.9% of hexaglycerol

Example 2

The same experiment was repeated with 50g of glycerol and 0.5g (1%) of sodium acetate anhydrous as the catalyst. The microwave oven was programmed to raise the temperature from ambient to 270°C in 2 minutes and this temperature was maintained for another 23 minutes, after which the cooling process was started to mark the end of reaction. The total reaction time was 25 minutes. The reaction product was worked-up as described in Example 1 and HPLC analysis revealed the compositions of each polymers of glycerol were as below. The treated polyglycerols yield was 83% and the conversion percentage of glycerol to polyglycerol was 74%.

Typical composition of glycerol polymers for reaction product of Example 2:

- ☐ 26.1 % of unreacted glycerol
- ☐ 28.9% of diglycerol
- ☐ 20.7% of triglycerol
- ☐ 12.7% of tetraglycerol
- ☐ 7.4% of pentaglycerol
- ☐ 4.2% of hexaglycerol

Example 3

The same experiment was repeated with 50g of glycerol and 0.5g (1 %) of sodium formate as the catalyst. The microwave oven was programmed to raise the temperature from ambient to 270°C in 2 minutes and this temperature was maintained for another 28 minutes, after which the cooling process was started to mark the end of reaction. The total reaction time was 30 minutes. The reaction product was also worked-up as described in Example 1 and HPLC analysis revealed the compositions of each polymers of glycerol were as below. The treated polyglycerols yield was 81 % and the conversion percentage of glycerol to polyglycerol was 79%.

Typical composition of glycerol polymers for reaction product of Example 3:

- ☐ 18.5% of unreacted glycerol
- ☐ 25.0% of diglycerol
- ☐ 22.0% of triglycerol
- ☐ 16.0% of tetraglycerol
- ☐ 11.0% of pentaglycerol
- ☐ 7.5% of hexaglycerol

Example 4

The same experiment was repeated with 50g of glycerol and 0.5g (1%) of tri-sodium citrate as the catalyst. The microwave oven was programmed to raise the temperature from ambient to 270°C in 2 minutes and this temperature was maintained for another 38 minutes, after which the cooling process was started to mark the end of reaction. The total reaction time was 40 minutes. The reaction product was also worked-up as described in Example 1 and HPLC analysis revealed the compositions of each polymers of glycerol were as below. The treated polyglycerol yield was 85% and the conversion percentage of glycerol to polyglycerol was 74%.

Typical composition of glycerol polymers for reaction product of Example 4:

- ☐ 26.0% of unreacted glycerol
- ☐ 29.1 % of diglycerol
- ☐ 20.6% of triglycerol
- ☐ 12.7% of tetraglycerol

- 7.7% of pentaglycerol
- 3.9% of hexaglycerol

Example 5

5 The same experiment was repeated with 50g of glycerol and 0.5g (1 %) of potassium citrate as the catalyst. The microwave oven was programmed to raise the temperature from ambient to 270°C in 2 minutes and this temperature was maintained for another 23 minutes, after which the cooling process was started to mark the end of reaction. The
10 total reaction time was 25 minutes. The reaction product was also worked-up as described in Example 1 and HPLC analysis revealed the compositions of each polymers of glycerol were as below. The treated polyglycerol yield was 84% and the conversion percentage of glycerol to polyglycerol was 72%.

Typical composition of glycerol polymers for reaction product of Example 5

- 15 □ 28.0% of unreacted glycerol
- 30.0% of diglycerol
 - 20.4% of triglycerol
 - 11.9% of tetraglycerol
 - 6.5% of pentaglycerol

20 □ 3.2% of hexaglycerol

Example 6

25 The same experiment was repeated with 50g of glycerol and 0.5g (1%) of sodium acetate trihydrate as the catalyst. The microwave oven was programmed to raise the temperature from ambient to 270°C in 2 minutes and this temperature was maintained for another 23 minutes, after which the cooling process was started to mark the end of reaction. The total reaction time was 25 minutes. The reaction product was worked-up as described in
30 Example 1 and HPLC analysis revealed the compositions of each polymers of glycerol were as below. The treated polyglycerol yield was 78% and the conversion percentage of glycerol to polyglycerol was 79%.

Typical composition of glycerol polymers for reaction product of Example 6

- 20.7% of unreacted glycerol
- 24.4% of diglycerol
- 21.0% of triglycerol
- 5 □ 15.7% of tetraglycerol
- 10.9% of pentaglycerol
- 7.27% of hexaglycerol

CLAIMS

1. A process for preparing oligomers and polymers of polyhydric alcohols from their monomers comprising heating the monomers using microwave irradiation in the presence of a catalyst, wherein the catalyst is a formate of lithium, sodium, potassium or other "hard" electrophiles or a combination thereof.
2. A process according to Claim 1 wherein the polymers of polyhydric alcohols are linear polyglycerols.
3. A process according to Claim 1 wherein the monomer is glycerol.
4. A process according to Claim 1 wherein the catalyst is a salt of alkaline metals and weak acids.
5. A process according to Claim 1 wherein the quantity of the catalyst used is 0.5 to 10 wt percent.
6. A process according to Claim 4 wherein the quantity of the catalyst used is 0.5 to 10 wt percent.
7. A process according to Claim 1 wherein the reaction is carried out at a temperature from 200 degree C. to 300 degree C.
8. A process according to Claim 1 wherein the reaction is carried out at a temperature from 250 degree C. to 270 degree C.
9. A process according to Claim 7 wherein the reaction time is from 15 to 40 minutes.
10. A process according to Claim 7 wherein the reaction time is 20 to 30 minutes.
11. A process according to Claim 1 wherein the irradiation is provided by a microwave equipment of 10W to 3,000 W.

12. A process according to Claim 1 wherein the irradiation is provided by a microwave oven, microwave generator or equipment.
13. A process according to Claim 1 wherein the degree of polymerisation of the monomer varies from $n=2$ to 10.
14. A process according to Claim 1 wherein the degree of polymerisation of the glycerol varies from $n=2$ to 10.
15. A process according to Claim 1 wherein the reaction is conducted at a pressure of 1 atmosphere.
16. A process according to Claim 1 wherein the catalyst is removed via treatment with an cationic ion exchanger.
17. A process for the preparation of polyglycerols in which glycerol is reacted in the presence of a catalyst at a temperature from 250 degree C. to 270 degree C for about 30 minutes by microwave irradiation.
18. A process according to Claim 17 wherein the water is removed from the resulting aqueous crude glycerols mixture by distillation.