

GLYCEROL TO POLYGLYCEROL: VALUE-ADDITION OF BIODIESEL BY-PRODUCT

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MPOB INFORMATION SERIES • ISSN 1511-7871 • JUNE 2010

MPOB TT No. 462

Crude glycerin of 75% to 85% is the major by-product from biodiesel plants. With the existing markets for glycerol, any increase in biodiesel production would indirectly skyrocket the glycerol supply. Moreover, the refining process and logistics of glycerol distribution will contribute to an increase in investment cost.

Over the recent years, MPOB has developed a technology for the direct utilization of crude glycerin containing 75% to 85% glycerol by converting the triol to polyglycerol via microwave irradiation (Figure 1).

yield. Conventional heating usually takes hours to complete. Based on the findings from our laboratory, it can be said that this technology is viable in the future for many other endothermic processes.

Polyglycerol is a mixture of glycerol oligomers. Polyglycerols are commonly prepared by mixing glycerol with an alkaline metal-based catalyst, such as sodium or potassium hydroxide, at elevated temperatures of 250°C-300°C.

The current simplified technology to produce polyglycerol is via the use of microwave irradiation (Figure 2) which can induce

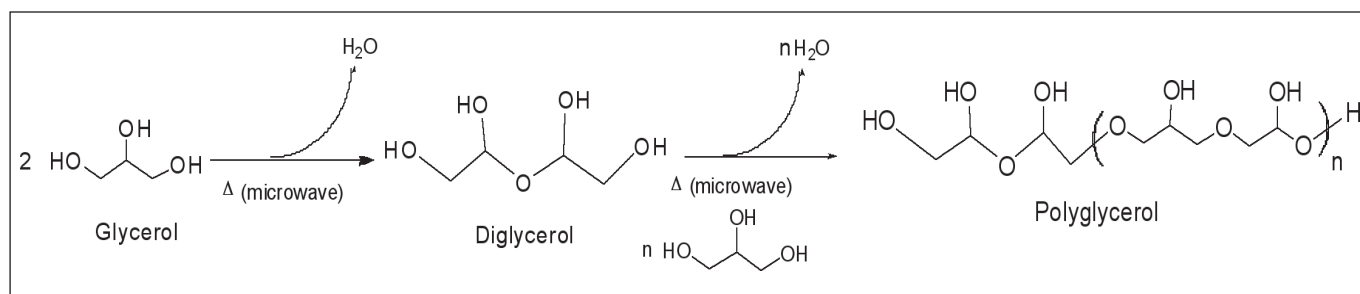


Figure 1. Microwave irradiation of crude glycerin to form diglycerol or polyglycerol.

TECHNOLOGY FOR PRODUCING POLYGLYCEROL

The Advanced Oleochemical Technology Division (AOTD) of MPOB has developed a technology to convert glycerol to polyglycerol, for direct usage of the inevitable biodiesel by-product, crude glycerin. Polyglycerol production via microwave technology offers a reaction with spectacularly low reaction time and, very often, improved

polymerization of crude glycerin from the biodiesel plant to polyglycerol, without any addition of a catalyst. The process has been filed for a patent with patent application No. PI20091872.

In our studies, five different samples of crude glycerol were obtained from different biodiesel plants, and the results after subjecting the samples to microwave irradiation are shown in Tables 1 and 2.

ISSN 1511-7871



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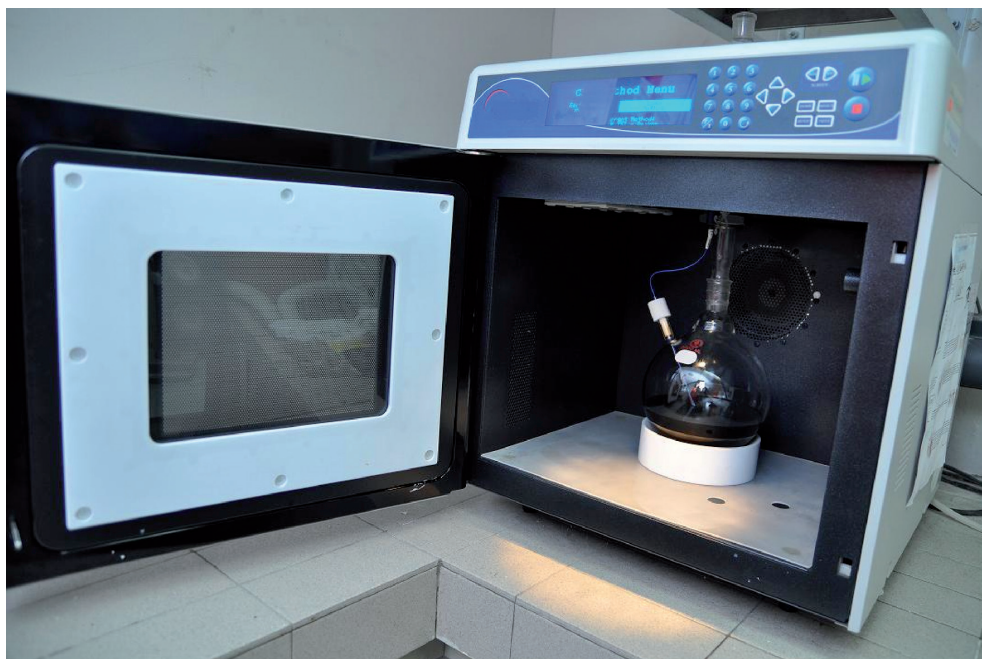


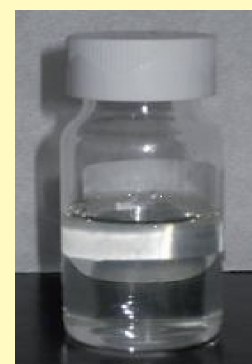
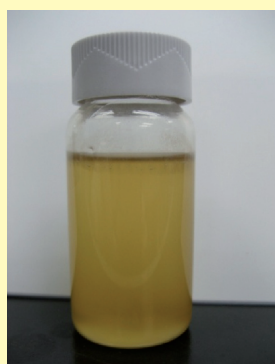
Figure 2. Bench top microwave reactor for open vessel organic synthesis.

TABLE 1. CONVERSION OF POLYGLYCEROL AND THEIR OLIGOMERS

Polyglycerol oligomer	A (%)	B (%)	C (%)	D (%)	E (%)
Diglycerol	4.983	39.957	31.605	55.077	47.99
Triglycerol	0	2.407	1.756	9.58	26.923
Tetraglycerol	0	0	0	1.598	14.012
Pentaglycerol	0	0	0	0	6.019
Conversion	4.98	42.36	33.36	66.26	94.94

TABLE 2. COMPOSITION OF PREPARED POLYGLYCEROL COMPARED WITH THAT OF A COMMERCIAL PRODUCT

Oligomer	Prepared polyglycerol (unbleached) (%)	Commercial polyglycerol (%)
Glycerol	1-5	0-30
Diglycerol	25-50	15-40
Triglycerol	25-30	10-55
Tetraglycerol	10-15	2-25
Pentaglycerol	0-6	5-15



With increased demand for biodiesel globally, there will also be available a huge amount of crude glycerin. Thus, this technology will greatly benefit the biodiesel industry where it can be integrated with the biodiesel plant.

APPLICATION OF POLYGLYCEROL

Based on the Technical Data Sheet and Material Safety Data Sheet of commercial polyglycerol in the current polyglycerol market, this material comprises mainly the following oligomer mixtures:

- diglycerol;
- triglycerol;
- tetraglycerol;
- hexaglycerol; and
- decaglycerol.

Polyglycerols can be converted to polyglycerol esters which can be used as an emulsifier in the food/cosmetic/plastic industries. Examples of polyglycerol manufacturers include Solvay (Bruxelles, Belgium) producing diglycerol and polyglycerol mixtures, and Sakamoto (Osaka, Japan) which produces diglycerol, tetraglycerol, hexaglycerol and decaglycerol.

A major potential market for polyglycerol is polyglycerol esters. Polyglycerol esters are important non-ionic surfactants. Their amphiphilic character enables their use in the stabilization of various suspensions and emulsions.

In cosmetics, they are used to emulsify, control viscosity and stabilize product formulae. They are incorporated into hair-styling gels, skin treatment gels, skin cleansers, baby creams, long-acting hand creams, moisturizing sunscreens and sun-protective sticks. Examples of the emulsifiers of polyglycerol type are:

- diglyceryl diisostearate in foundation creams;
- diglyceryl monolaurate in make-up removing skin cleansers; and
- diglyceryl monooleate in baby creams.

In the food industry, polyglycerol esters are used as emulsifying agents in the production of fine bakery products, chewing gum and in fat replacement products. For example, polyglycerol

polyricinoleate is a strong lipophilic water in oil emulsifier. It is a highly viscous liquid, insoluble in water and ethanol, but soluble in fats and oils. It is used as a viscosity-reducing agent in chocolate.

ADVANTAGES

1. The production process is simplified in two ways:
 - no addition of catalyst is needed; and
 - microwave-induced reaction.
2. Helps to make the biodiesel industry more sustainable.
3. Provides an outlet for crude glycerin produced from biodiesel plants.

POLYGLYCEROLS MARKET

Worldwide, the market for polyglycerols was projected at 40 000 t at a price of USD 4-USD 5 kg⁻¹ in 2006. Polyglycerols, predominantly polyglycerol esters, have captured the biggest share in the market for emulsifiers in which the price of polyglycerol esters over the years have been increasing and is expected to continue showing the same growth trend in near future (Table 3).

TABLE 3. AVERAGE PRICE OF POLYGLYCEROL ESTER AND POLYGLYCEROL METHYL ESTER EMULSIFIERS

Year	Average price (USD kg ⁻¹)	Price growth rate (%)
2003	3.59	-
2004	3.88	8.0
2005	4.19	8.0
2006	4.50	7.5
2007	4.82	7.0
2008	5.15	7.0
2009	5.48	6.3
2010	5.79	5.8
2011	6.08	5.0
2012	6.36	4.5
2013	6.64	4.5

Source: Frost and Sullivan (2006).

ECONOMIC ANALYSIS

The economic analysis was based on 100 litres per hour, microwave reactor with reaction production capacity of 580 t per year with 80% conversion of glycerol to polyglyserol (calculation was based on the price of crude glycerol at USD 100 t⁻¹).

Return on investment = 25.61%

Payback period = 3.9 years

CONCLUSION

Crude glycerin is the inevitable by-product of biodiesel production. It can be directly converted into polyglycerol using microwave irradiation. Polyglycerol is a value-added intermediate. It can be further converted into polyglycerol ester which is widely used as an emulsifier in the food, cosmetic and personal care product industries. This technology will help to add value to the crude glycerol produced from the biodiesel industry.

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