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Chapter

Glycerol Conversion to Diglycerol via Etherification under Microwave Irradiation

Muhammad Ayoub, Wan Jie Wei, Manzoor Ahmad, Ranitha Mathialagan, Sarah Farrukh, Mohammed Danish, Sami Ullah and Salman Raza Naqvi

Abstract

According to Grand View Research in polyglycerol market size, demand for diglycerol is expected to grow by 50% from 2012 to 2022 due to its extensive use in various industries, thus validating the importance and value addition of producing diglycerol. Due to the volatility of refined glycerine market price and increasing demand of diglycerol, research has been conducted to upgrade glycerol via various processes. Etherification is a single-step process of catalytic conversion of glycerol into polyglycerols, involving the condensation of two glycerol molecules to form the simplest oligomer which is diglycerol with linear, branched, or cyclic isomers. Thus, this chapter will discuss on the methods of synthesizing diglycerol followed by the type of catalyst to be used. These include homogenous and heterogenous catalyst with their subdivision of acid and base type, respectively. Besides, this chapter does include on the method for the etherification process where it highlighted the advantage of advance technology microwave irradiation over conventional heating.

Keywords: diglycerol, etherification, microwave, yellow glycerine, industrial

1. Introduction

Glycerine, also called glycerol (propane-1,2,3-triol, C₃H₈O₃), occurs as the backbone in triglycerides which are the main constituents of all vegetable and animal fats and oils. It is colorless and odorless, has sweet taste, and is very viscous and hygroscopic [1, 2]. Glycerol is a key ingredient in personal care product due to its property of acting as humectants, solvents, moisturizer, as well as an additive to make coatings. Glycerol is currently produced from biodiesel transesterification, saponification, and hydrolysis processes in fatty acid and soap production [3]. Among these, biodiesel transesterification is the biggest crude glycerol generation sector, contributing up to 67% of the total crude glycerol production, followed by high pressure splitting (17%) and soap production (<10%) [4].

Due to the growing biodiesel demand as substitution to petroleum-based diesel, the production of crude glycerol as by-product from this process is also increased. For every 1 ton of biodiesel produced, approximately 100 kg of glycerol will be generated [5]. The crude glycerol generated contains many impurities such as methanol, organic and inorganic salts, water, unreacted triglycerides, soap, fatty acid, etc. Hence, for large-scale biodiesel manufacturers, the plants are normally equipped with crude glycerol refining facilities to produce glycerol with purities up to 95.5 and 99% [3].

Generally, there are three types of glycerol, namely, crude glycerine, technical grade glycerine, and refined glycerine. The process of refining glycerine is a complex process which involves distillation, bleaching, acidification, and several intermediate steps. In the distillation step, refined glycerine is obtained from the side draw of the distillation column and then subsequently bleached and deodorized to achieve the refined grade. Technical grade glycerine, also called yellow glycerine, is obtained from the top of the column with some impurities such as water, fatty acids, soap, etc. [2]. **Figure** 1 shows the general process flow of glycerine refining. According to MarketWatch 2018, the global glycerine market is expected to reach approximately 6200 metric tons by 2024 from 3550 metric tons in 2016, resulted from the growth in bio-renewable chemicals, biodiesel production, and wide range of applications. However, with regard to the market price, technical grade glycerine is cheaper than the refined glycerine which are approximately RM4400 and RM5400 per metric ton, respectively, as reported by Oleoline (2017).

Furthermore, glycerol can be used as a starting material for the synthesis of value-added chemicals via catalytic conversion such as hydrogenolysis to propanediol and ethylene glycol, dehydration to acrolein, fermentation to propane-1,3-diol, thermal reduction into syngas, etherification to fuel oxygenates, conversion into glycerol carbonate, and synthesis of epichlorohydrin [6]. Among these, the etherification of glycerol into polyglycerols particularly diglycerol (DG) and triglycerol (TG) is gaining more interest in the recent research due to their possibility in controlling the hydrophilic–lipophilic balance (HLB) which is highly important as additive to food and pharmaceutical industries, lubricants, stabilizers, dispersants, plasticizers, etc. [6]. According to Grand View Research in polyglycerol market size, the demand for diglycerol and triglycerol is expected to grow by 50% from 2012 to 2022. The global diglycerol demand is expected to grow at a CAGR of 5.3% due its extensive use in various industries, thus validating the importance and value addition of producing diglycerol.

Due to the volatility of refined glycerine market price and increasing demand of polyglycerol especially the shortest chain oligomer which is diglycerol, research has been conducted to upgrade glycerol via various processes such as pyrolysis, epichlorohydrin, and catalytic etherification to produce polyglycerols. Etherification is a single-step process of catalytic conversion of glycerol into polyglycerols, involving the condensation of two glycerol molecules to form the simplest oligomer which is diglycerol with linear, branched, or cyclic isomers. Further reaction yields tri-, tetra-, and higher oligomers. Short-chain oligomers are preferred. Therefore, the

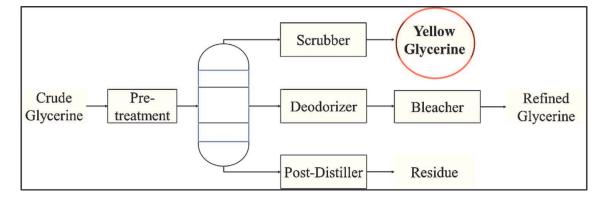


Figure 1. *General process flow of glycerine refining.*

etherification of glycerol under controlled conditions is required [7]. The etherification method has potential to replace the conventional epichlorohydrin route of producing polyglycerols which is relatively complex and involves in the production of toxic intermediate. Polyglycerols can be produced from different raw materials such as crude glycerine, yellow glycerine, as well as pure glycerine [7–9]. Hence, the economical production of glycerol derivatives is directly related with the quality of glycerine feedstocks and prices.

With regard to the heating method, microwave irradiation has been increasingly popular as a heating method for organic reaction. It had been proven to be more effective than the conventional water bath heating [10]. Various benefits of microwave irradiation included internal rapid heating that reduced the reaction time which compensates its higher power consumption. Besides, efficient and uniform heating that enables good temperature control can be achieved via microwave heating.

2. Glycerine conversion

2.1 Existing diglycerol synthesis method

2.1.1 Laboratory-scale routes

On small scale, pure diglycerol is produced via direct synthesis methods in which diallyl ether is used as a primary reactant [1]. Diallyl ether is accessible by the reaction between allyl chloride and allyl alcohol in inert solvents under hydrogen chloride release. Direct hydroxylation of this product can be performed with peroxyformic acid, CH₂O₃, or permanganate at 40°C under safety precautions for 4.5 hours. However, several additional steps are needed for neutralization, filtration, derivatization, and fractional distillation which are required for the isolation of diglycerol and triglycerol. The isolation of diglycerol can be done using neutralization with barium hydroxide solution, centrifugation to separate the solid, digestion of the product in absolute ethanol, and fractional distillation under reduced pressure.

2.1.2 Thermal conversion of glycerol

The thermal reaction for glycerol oligomerization is conducted at a certain temperature under inert protecting reactor condition [1]. For selective reaction, pure glycerol up to 99% purity should be used. Commonly, before the use of the oligomeric products for further reactions, a distillation is needed to remove unconverted glycerol. Reaction temperature, basicity, and organic impurities would affect the glycerol oligomerization. For pure thermal conversion of glycerol without the addition of catalyst, temperature is normally set above 200°C. However, at reaction temperature higher than 290°C, side products with strong smelling are formed. At 180°C (low temperature) with the addition of alkali catalyst, the formation of diglycerol from glycerol is observed but at low conversion of glycerol.

2.1.3 Epichlorohydrin method

The epichlorohydrin method of producing polyglycerol is commonly applied. It involves basic hydrolysis by sodium hydroxide, led to the formation of intermediate product, namely, glycidol and glycerol, and it will react with unconverted epichlorohydrin or glycerol to diglycerol [6]. Further separation and purification of products are required. Residue glycerol will be separated, and then water has to be removed from the raw diglycerol, and, finally, the product has to be subjected to a fine distillation. The reaction of glycidol or epichlorohydrin with glycerol has in common that the coupling OH groups are not confined to the terminal positions but also the middle OH groups of glycerol can be involved as well. This leads to the formation of primary or secondary dimer of glycerol.

2.1.4 Catalytic reaction method

The etherification reaction of glycerol to produce value-added diglycerol has been extensively studied either using homogeneous or heterogenous alkali or acid catalysts. The etherification reaction is normally conducted under solvent-free condition for economical and environmental reasons [7]. Etherification is a condensation process whereby two glycerol molecules will react to form ether bond in between the molecules by removing water molecule. This reaction is also called etherification since the final product is in ether form as shown in **Figure 2**. Glycerol oligomers can be in linear, branched, or cyclic form [11]. The formation of different isomers is affected by the reaction conditions such as temperature, time, catalyst type, catalyst loading as well as the starting raw material for diglycerol synthesis. Diglycerols are mostly obtained from the oligomerization of glycerol catalyzed by acid or based catalysts.

2.2 Homogeneous catalyzed reaction for selective diglycerol

2.2.1 Homogeneous acid catalyst

The reaction by homogeneous acid catalyst is promoted by the protonation of one of the glycerol hydroxyl groups: a mechanism of SN_1 as shown in **Figure 3**. A carbocation is formed by splitting off a water molecule, followed by nucleophilic attack of a hydroxyl group of another glycerol molecule. Then, the formed ether is

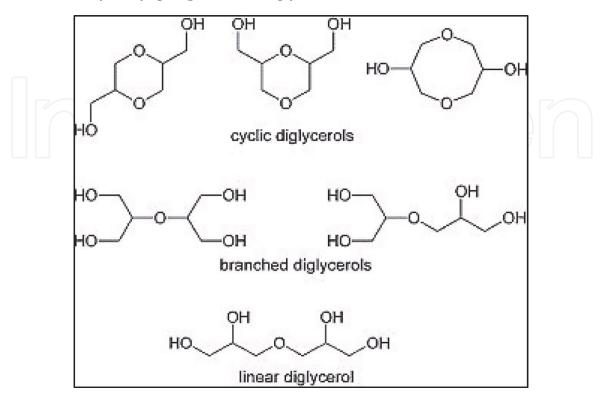


Figure 2. *Etherification of glycerol to polyglycerols.*

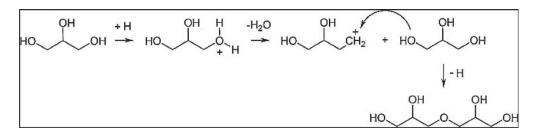


Figure 3.

 SN_1 -type mechanism for glycerol oligomerization in acid-catalyzed homogeneous reaction.

deprotonated, yielding the respective diglycerol [1]. Acid-catalyst oligomerization used sulfuric acid at 280°C in 2 hours giving more than 90% conversion of glycerol, and the main oligomers were triglycerol and tetraglycerol which only make the 20% of overall component, showing other side products were dominant in the reaction which were hardly identified [6].

Reported studies suggest that homogeneous acid-catalyzed reaction is generally fast but not selective for diglycerol. This could be due to the dehydration or oxidation of glycerol as secondary reactions to other undesired products. These secondary reactions may also result in the deterioration of the main product quality by changing its color, making the final product darker in appearance.

2.2.2 Homogeneous base catalyst

The reaction with glycerol conversion under basic homogeneous catalyst is proposed to follow an SN_2 mechanism as shown in **Figure 4**. In SN_2 , the interaction of the base OH with glycerol weakens one of the glycerol OH bonds and enhances nucleophilic character of the hydroxyl oxygen. The attack of this polarized glycerol to a carbon of a second glycerol with simultaneous split off water results in diglycerol.

Several homogeneous bases have also been studied as catalysts in glycerol etherification. Depending on their basicity and solubility in glycerol, the following order of activity was reported under reaction temperature of 260°C at 4 hours with 2.5 mol% of catalyst:

K2CO3 > Li2CO3 > Na2CO3 > KOH > NaOH > CH3ONa > LiOH > MgCO3 > CaCO3.

Based on solubility measurements, the higher activity of carbonates than that of hydroxides was indeed ascribed to a better solubility of the former in glycerol and in the polyglycerol mixture at elevated temperature [6]. However, there are several studies presented that contradict the results from the proposed theory on solubility. A study conducted by [9] of glycerol conversion using Cs₂CO₃, CsOH, and CsHCO₃ showed 20% glycerol conversion and 100% diglycerol selectivity; hence, different anions did not alter the reaction characteristics. From the research carried out by

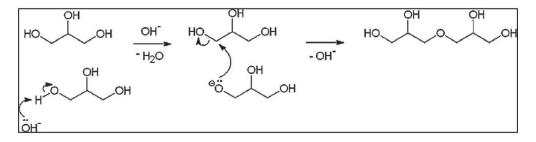


Figure 4. SN_2 -type mechanism for glycerol oligomerization in base-catalyzed homogeneous reaction.

[7], their studies reflected that the pH of the mixture of catalyst with glycerol which increased in the order LiOH, NaOH, KOH, and Na₂CO₃ was the main factor of high glycerol conversion and diglycerol selectivity. One hundred percent glycerol conversion was achieved for LiOH and NaOH catalysis system with 21 and 18% diglycerol selectivity, respectively. This could be resulted from the nature of lithium metal as the most active metal due to highest alkalinity, smallest ionic size, and highest atomic electronegativity [7].

Raw material choice on polyglycerol production is also very crucial in polyglycerol generation. A study done by [8] argued that polyglycerol production can be carried by the self-polymerization of crude glycerol which contained different amounts of soap (as homogeneous-based catalyst) which was originally presented in the crude glycerol samples. The experiment was carried out at 260°C under microwave heating; within 1 hour, the sample of soap with a highest soap content of 12.5% gave the highest conversion (94.94%) with 47.99% diglycerol. This study supported the claim by [7], whereby the higher the pH, the higher is the conversion and diglycerol selectivity. Besides, they also found that the processes with different feedstocks affected the amount of soap contained in the crude glycerol, preferably the refined, bleached, deodorized palm oil (RBDPO) which generated the highest amount of soap, creating a favorable condition for selfpolymerization.

The shortcomings from homogeneous catalysis system include low selectivity to small-size polyglycerols which is the desired product of polyglycerols; uncontrollable oligomerization of glycerol which produces larger polyglycerols together with smaller polyglycerols would result in separation issue.

2.3 Heterogeneous catalyzed reaction for selective diglycerol

Recently, the main focus on catalytic etherification is on the implementation of heterogeneous catalyst in the etherification reaction to overcome the shortcomings of using homogeneous catalyst whereby the reactions are performed on solid materials of limited solubility [1]. Mesoporous solids modified by cesium impregnation or exchange lead to the best selectivity and yield to diglycerol in which 100% of diglycerol was produced after 10 hours reaction time [12]. The etherification activity was improved by the impregnation of LiOH with acid-treated montmorillonite K-10 (clay MK-10) [13]. Researchers reported that the clay Li/MK-10 catalyst gave a favorable result in selectively producing diglycerol which yielded 53% with high glycerol conversion of about 98%. However, the drawbacks of using heterogeneous catalyst are the leaching of metal from solid support into the liquid mixtures and instability of the solid support, resulting in dropping in efficiency to cater the reaction.

2.4 Microwave and conventional heating

Microwaves are electromagnetic waves which consist of both electric and magnetic fields that fall within 0.3–300 GHz on electromagnetic spectrum with wavelengths ranging from 0.01 to 1 m. Within the specific frequency range, the microwave transmits energy between 1.24×10^{-6} and 1.24×10^{-3} eV. **Table 1** shows the energy of different chemical bonds and microwaves [14]. With the energy lower than the Brownian motion, microwave will not be able to induce chemical reactions through bond breaking.

Microwave heating is a direct heating method which is highly dependent on the properties of materials to convert electromagnetic to heat energy. The two ways of inducing heat into a systems via microwave are dielectric heating and magnetic loss

heating; however, based on the publications, researchers are mainly focus on studying the dielectric heating effects and mechanisms because this heating effect is more significant. Dielectric heating occurs due to the dielectric properties on the reacting medium. For example, materials with high dielectric constant tend to absorb microwave; however, poor dielectric property compounds are poor electromagnetic wave absorber. Hence, microwave is highly applied in organic reactions.

In conventional heating, heat is transferred through conduction and convection in which the heat is transferred from the sides/surface of a substance, then only travel to the center of targeted heating medium. This heating method is dependent on the heating flask properties such as thermal conductivity, specific heat capacity, density, etc. Hence, the portion of heat will be loss to the environment during heating. When compared to microwave heating, the heating duration using microwave to achieve the same temperature could be dramatically reduced. **Figure 5** shows the heating mechanism for both conventional heating and microwave heating.

Microwave radiation serves as an alternative to conventional heating especially in organic synthesis. The advantages of microwave heating over conventional heating are accelerating chemical reactions and promoting higher conversion and selectivity and low energy consumption as reported by [14] with respect to the same operating conditions under microwave heating. Plenty of studies have been carried out on the application of microwave in organic synthesis, for example, reactions in solvent-free condition, polymer synthesis, homogeneous and heterogeneous catalysis, medicinal and pharmaceutical chemistry, etc. [15].

Bonding and microwave	Energy (eV)
Brownian motion at 37°C	$2.7 imes10^{-3}$
Biological compound	13.6
Covalent bond	5
Hydrogen bond	2
Van der Waals intermolecular interactions	<2
Microwave at 0.3 GHz	$1.24 imes10^{-6}$
Microwave at 2.45 GHz (domestic oven)	$1 imes 10^{-5}$
Microwave at 300 GHz	$1.24 imes 10^{-3}$

Table 1.

Energy of different bonds and microwaves.

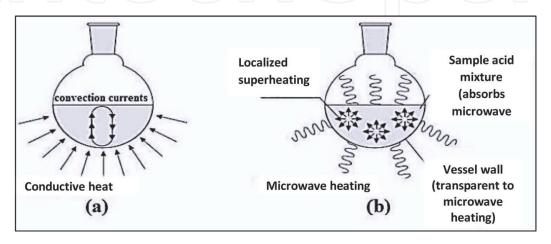


Figure 5. *Heating mechanisms for (a) conventional heating and (b) microwave heating.*

Theories that are applied to explain the effect of microwave in enhancing a reaction are based on thermal and nonthermal effects as presented by [14] in **Table 2**.

Most of the studies on microwave effects describe the presence of hot spots or localized heating which enhances the chemical reactions due to direct adsorption of radiation by the polar molecules. Microwave energy is transferred through the relaxation of polar molecules, thus promoting molecular friction and collision [10]. As reported by [15], the hot spot will possess higher energy at the active sites, promoting the activities of the species adsorbed on the catalyst surface, whereas [16] presented that the conversion of hydrogen sulfide is higher than the theoretical equilibrium conversion; however, the results from conventional heating are similar to the theoretical value. They claimed that the reaction temperature at some site in the catalyst bed was much higher than the average temperature measured. However, studies by [14] illustrated that the occurrence of hot spot on catalyst surface is more likely to lower the catalytic activities, hence reducing the productivity. For an exothermic reaction, for example, the desulfurization, both microwave and conventional, provides similar conversion at the same operating conditions. Further increment in temperature in microwave system would cause the conversion to drop (lower than conventional heating), due to the shifting of equilibrium to less favorable reactions [16].

Besides localized heating effects, decreasing in the activation energy and improving the pre-exponential factor are the two main factors in enhancing microwave-assisted organic synthesis. When inducing microwave, a portion of the radiation heats up the system due to microwave thermal effects; another portion directly interacts with chemical or catalytic reaction system to reduce the activation energy, changing the interior energy level of molecules. The increment in the preexponential factor is due to the effective collision between molecules assisted by electromagnetic wave which change the movement of the molecules from disordered motion to ordered motion [17].

Even though in most cases microwave heating enhances the reactions, in the reaction with high sensitivity to the temperature change especially in a strong exothermic reaction, conventional heating would be preferred. The study in Fischer glycosidation showed a higher conversion under conventional heating which may be due to the higher overall reaction time, and the reaction temperature is reached smoothly. The reaction under conventional heating does not present localized overheating which can be found in microwave heating. Localized overheating in microwave was observed from the temperature overshoot above the desired temperature, causing glucose decomposition [18].

For the etherification reaction, most of the researches were conducted by conventional heating, and typical reaction times were longer than 8 hours. Microwave radiation is proven to be a more effective heating method in the etherification of glycerol. The required reaction time to produce targeted polyglycerols facilitated by

Thermal effects	Nonthermal effects
Dipolar polarization	$K = A \exp(-Ea/RT)$
Ionic conduction	Enhancement in collision probabilities
Uniform heat distribution	Decrease in activation energy
Specificity for polar molecule	Hot spots
Effect increase with polarity	High localized microscopic temperatures

Table 2.

Microwave heating mechanisms via thermal and nonthermal effects.

the microwave irradiation was much shorter than the etherification carried out by conventional heating which required at least 6 hours, whereas it took only 1 hour for microwave heating.

3. Conclusion

Microwave irradiation-assisted heating found to be a cost-efficient technology to be applied for the biodiesel conversion into polyglycerol. The application of modified heterogenous base catalyst could minimize the waste besides being compatible for the reaction of biodiesel waste into polyglycerol. Besides, it has provided insight on the oligomerization reaction of glycerol to maximize the yield of the valuable di-, tri-, and tetraglycerol oligomers for numerous applications with current industrial demand.

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References

[1] Martin A, Richter M.
Oligomerization of glycerol—A critical review. European Journal of Lipid
Science and Technology. 2011;113(1):
100-117. DOI: 10.1002/ejlt.201000386

[2] Mbamalu VC. Glycerin and the Market. Chattanooga, Tennessee:University of Tennessee at Chattanooga;2013

[3] Anitha M, Kamarudin SK, Kofli NT. The potential of glycerol as a valueadded commodity. Chemical Engineering Journal. 2016;**295**:119-130. DOI: 10.1016/j.cej.2016.03.012

[4] Kong PS, Aroua MK, Daud WMAW. Conversion of crude and pure glycerol into derivatives: A feasibility evaluation. Renewable and Sustainable Energy Reviews. 2016;**63**:533-555. DOI: 10.1016/ j.rser.2016.05.054

[5] Barros FJS, Moreno-Tost R, Cecilia JA, Ledesma-Muñoz AL, de Oliveira LCC, Luna FMT, et al. Glycerol oligomers production by etherification using calcined eggshell as catalyst. Molecular Catalysis. 2017;**433**:282-290

[6] Sivaiah MV, Robles-Manuel S, Valange S, Barrault J. Recent developments in acid and basecatalyzed etherification of glycerol to polyglycerols. Catalysis Today. 2012; **198**(1):305-313

[7] Ayoub M, Khayoon MS, Abdullah AZ. Synthesis of oxygenated fuel additives via the solventless etherification of glycerol. Bioresource Technology. 2012;**112**:308-312. DOI: 10.1016/j.biortech.2012.02.103

[8] Din NSMNM, Idris Z, Kian YS,
Hassan HA. Preparation of polyglycerol from palm-biodiesel crude glycerine.
Journal of Oil Palm Research. 2012;
25(3):289-297 [9] Richter M, Krisnandi Y, Eckelt R, Martin A. Homogeneously catalyzed batch reactor glycerol etherification by CsHCO3. Catalysis Communications. 2008;**9**(11–12):2112-2116. DOI: 10.1016/ j.catcom.2008.04.007

[10] Teng WK, Ngoh GC, Yusoff R, Aroua MK, Heng JS. Microwave assisted solvent-free catalytic transesterification of glycerol to glycerol carbonate. International Scholarly and Scientific Research and Innovation. 2015;**9**(9): 1140-1143

[11] Ruppert AM, Meeldijk JD,
Kuipers BW, Erne BH,
Weckhuysen BM. Glycerol
etherification over highly active
CaO-based materials: New mechanistic
aspects and related colloidal particle
formation. Chemistry. 2008;14(7):
2016-2024

[12] Barrault J, Clacens JM, Pouilloux Y. Selective oligomerization of glycerol over mesoporous catalysts. Topics in Catalysis. 2004;**27**(1):137-142

[13] Ayoub M, Abdullah AZ. Diglycerol synthesis via solvent-free selective glycerol etherification process over lithium-modified clay catalyst.
Chemical Engineering Journal. 2013;225: 784-789

[14] Nomanbhay S, Ong MY. A review of microwave-assisted reactions for biodiesel production. Bioengineering (Basel). 2017;4(2):57

[15] Das BC, Bhowmik D, Chaudhuri S.Microwave system. The PharmaInnovation. 2012;1(6):1-16

[16] Zhang X, Hayward DO,Mingos DMP. Effects of microwave dielectric heating on heterogeneous catalysis. Catalysis Letters. 2003;8(1-2): 33-38

[17] Zhou J, Xu W, Wang Z, Luo Y, Gao L, Yin C, et al. A new type of power energy for accelerating chemical reactions: The nature of a microwavedriving force for accelerating chemical reactions. Scientific Reports. 2016;**6**: 25149

[18] Ceron-Camacho R, Aburto JA, Montiel LE, Martinez-Palou R.
Microwave-assisted organic synthesis versus conventional heating. A comparative study for Fisher Glycosidation of monosaccharides.
Comptes Rendus Chimie. 2013;16(5): 427-432

