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Glycerol: solvent and building block of choice for microwave and ultrasound irradiation procedures

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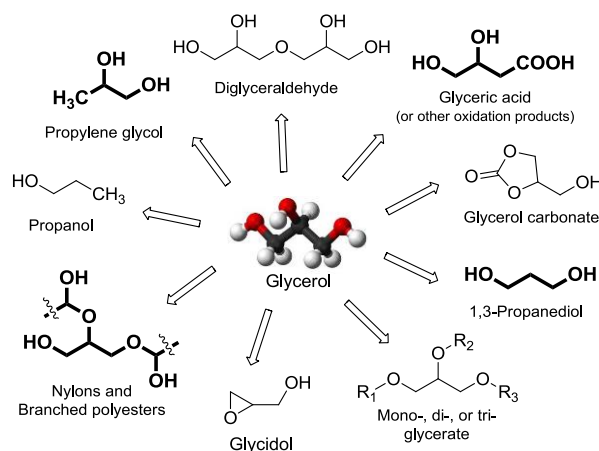
Glycerol has the potential to be both an excellent renewable solvent in modern chemical processes and a versatile building block in biorefineries. Both of these potential applications may be made easier and more convenient by microwave and/or ultrasound irradiation. As glycerol is a nontoxic, biodegradable compound, it will provide important environmental benefits to new platform products. Furthermore, significant markets in polymers, polyethers, fuel additives, nanoparticles and other valuable compounds may well be opened up by cutting down the high purification cost of glycerol. The aim of this review is to highlight the best literature examples of glycerol being used, either as solvent or as a reagent, to give interesting results under microwave or ultrasound irradiation.

1. Introduction and background

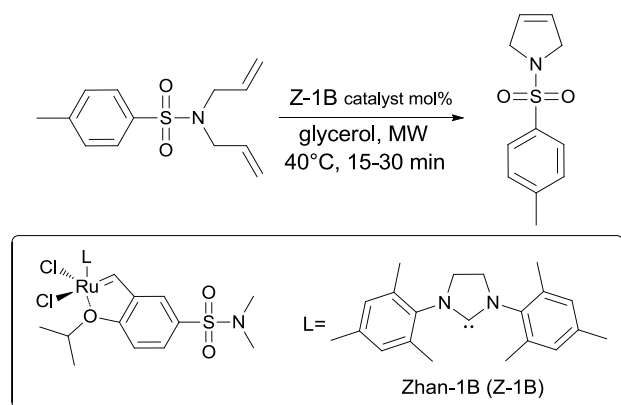
The use of green solvents and building blocks from renewable resources has been the subject of enormous interest in recent years. Glycerol is the main co-product of biodiesel and oleochemical production, only 20% of world production is prepared synthetically from the chemical conversion of propylene. With annual world production at over 1×10^6 tonnes, it can truly be considered a 21st century commodity. Unfortunately, crude glycerol from transesterification is a brown mixture that contains water and other impurities and requires expensive purification before it is suitable for new product technologies. R&D organizations worldwide are dedicating enormous amounts of energy to reducing glycerol refining costs by trying to optimize fixed base and acid-base esterification catalysts. The Merck Index 11th Edition had already reported over 1500 different uses for glycerol by 1945.¹ Today, although many other uses have been developed, most product markets are small and fragmented, reflecting glycerol's relatively high price. If prices drop, glycerol might become a major building block for the biorefinery. Fig. 1 describes the wide potential of glycerol as a starting material. Although glycerol exhibits promising features as a sustainable solvent for liquid-phase catalytic and non-catalytic organic syntheses, its use has several drawbacks which include high viscosity at room temperature and the low solubility of highly hydrophobic compounds and gases in it (i.e. H_2 , O_2). These factors limit its mass transport capabilities. These limitations can be overcome using high-intensity ultrasound (US) and microwaves (MW), in a stand-alone or combined manner,² to enhance heat and mass transfer, and hence, accelerate reaction rates.³ Both techniques have emerged in recent years and have taken up the roles of new and irreplaceable tools in green organic synthesis.⁴

Fig. 1: Glycerol derivatives.

The intrinsic characteristics of glycerol, such as its low vapour pressure, high-boiling point, high dielectric constant and a

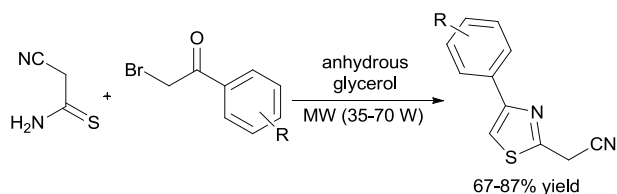


polarity value that is similar to DMSO or DMF, make it a suitable solvent for MW irradiation, where the heating characteristics of a solvent play a crucial role. For the sake of clarity, some discussion follows on what makes glycerol so potentially appealing in either microwave or ultrasound fields. Microwave dielectric heating is based on the ability of a specific reagent or solvent to absorb such a radiation and convert it into heat at a given frequency and temperature. [C. Kappe, *Angew. Chem. Int. Ed.*, 2004, **43**, 6250-6284] The key parameter is the so-called loss factor or loss tangent ($\tan\delta$), which is the quotient between the dielectric loss (ϵ'') accounting for the efficiency in converting electromagnetic radiation into heat, and the dielectric constant (ϵ') that merely describes molecular polarization by the electric field. High $\tan\delta$ values are indicative of high MW absorption and rapid heating. As expected, polar molecules (alcohols or DMSO are prototypical) exhibit high loss factors (> 0.5), even though water has a rather modest $\tan\delta = 0.123$ at 2.45 GHz, while substances of low polarity have $\tan\delta < 0.1$ and those without a permanent dipole moment will be transparent to MW. [C. Gabriel, S. Gabriel, E. H. Grant, B. S. J. Halstead and D. M. P. Mingos, *Chem. Soc. Rev.*, 1998, **27**, 213-223] From a synthetic



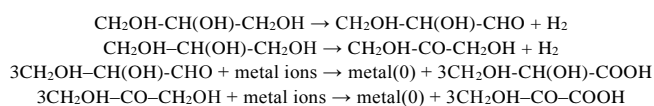
Scheme 4

substituted 2-bromoacetophenones under MW irradiation using glycerol as the solvent (Scheme 5). The fast procedure (around 4 min) gave excellent yields and high purity products after a simple work-up. This approach can be applied to the preparation of a variety of 2-cyanomethyl-4-phenylthiazoles.



Scheme 5 Preparation of substituted 2-cyanomethyl-4-phenylthiazoles under MW.

Grace *et al.* (⁹) have studied the use of glycerol as a reducing agent and solvent for the synthesis of PVP (polyvinylpyrrolidone)-protected metal nanoparticles. Pt, Pd, Ag and ruthenium-PVP nanoparticles have been synthesized under reflux and MW conditions. The general mechanism of metal reduction in glycerol is depicted in scheme 6.



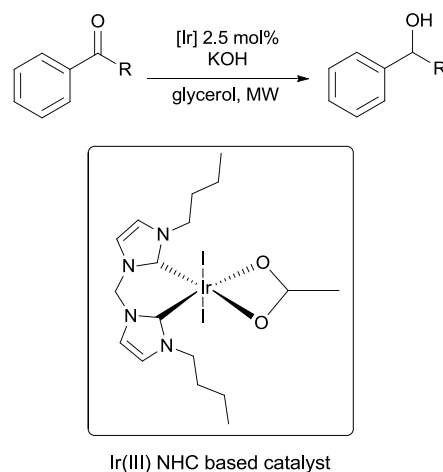
Scheme 6 mechanism of metal reduction in glycerol

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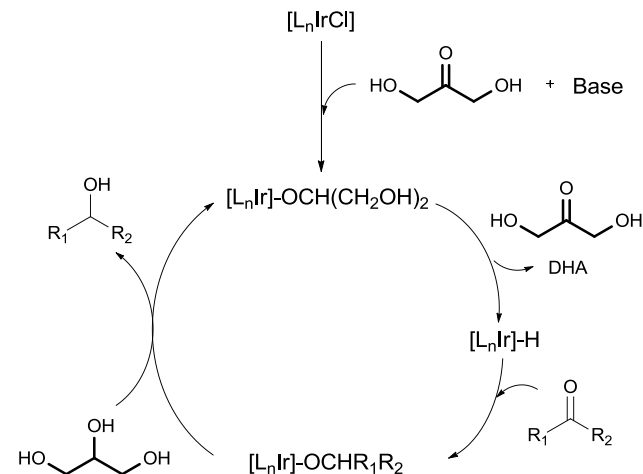
When the reaction was carried out under reflux, the average Pd, Ag and Ru particle size was *ca.* 6 nm, whereas under dielectric heating, particle size was smaller than *ca.* 2 nm. In general, the faster the reduction reaction proceeded, the smaller the formed particles were. It was observed that the palladium particles grew anisotropically when the reaction was carried out under MW. This observation is based on two important factors. There is competition between the nucleation period and the arrangement of PVP moieties around Pd particles which, in turn, depends on the time and speed of the reaction. In the case of MW heating, nucleation takes place along any plane, whereas in the reflux method, it occurs in all planes and axes resulting in a uniform spherical shape.

Four Ir(I) and Ir(III) N-heterocyclic carbene (NHC)-based complexes with 3,4,5-trimethoxybenzyl N-substituents have

been used by Colacino *et al.* (¹⁰) as catalysts in the reduction of aldehydes and ketones in glycerol. Their catalytic properties were compared with those of previously reported iridium complexes used in the transfer hydrogenation reaction, where glycerol is both solvent and hydrogen donor, under MW, US and oil bath conditions (Scheme 7). The formation of spherically shaped Ir(0)-nanoparticles in both glycerol dielectric heating and sonochemical conditions was demonstrated. The new Ir(III) complexes proved to be most efficient in the reduction of ketones, while the Ir(I) complexes are more active in the reduction of aldehydes.



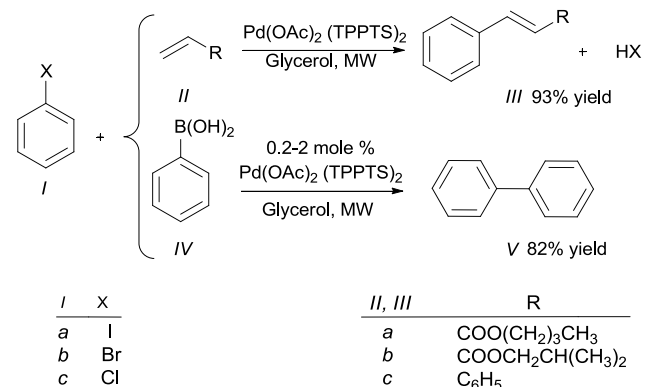
Scheme 7 Iridium-catalyzed transfer hydrogenation reactions of carbonyl compounds.



Scheme 8 Plausible Mechanism for Iridium-Catalyzed Transfer Hydrogenation Reactions in Glycerol.

Wolfson *et al.* (¹¹) have reported successful MW-assisted Heck and Suzuki reactions in glycerol using Pd(OAc)₂ bis(tris(3-sulphophenyl)phosphine trisodium salt), (TPPTS)₂, as the catalyst and Na₂CO₃ as the base (Scheme 9). Although the experiments were conducted in a domestic MW oven, the reaction mixture temperature was strictly monitored (from 26 °C up to 89 °C in 5 min, or up to 117 °C in 10 min). The product was easily isolated in high yields via extraction with glycerol-immiscible solvents which also enabled the catalyst to be recycled.

It is known that glycerol can act as a reducing agent in the fabrication of noble nanometals, such as Au, Pt, and Pd, under MW irradiation (Kou *et al.*).¹² A number of surfactants, such as cetyltriethylammonium bromide (CTAB), polyvinylpyrrolidone (PVP), and sodium dodecyl sulfate (SDS), have been used to synthesize samples of various morphologies.



Scheme 9 Palladium-catalyzed Heck and Suzuki couplings of halobenzenes with butyl acrylate and phenylboronic acid in glycerol.

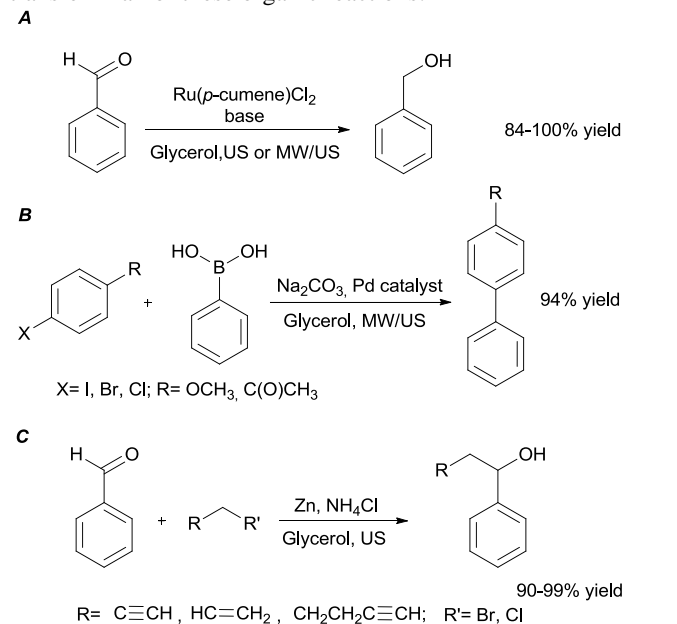
In the presence of CTAB, Au nanosheets were formed in 2 min and their size was controlled by the MW irradiation time. When the reaction time was 2 min, the side length of hexagonal nanosheets was about 1-1.5 μm which could be enhanced by prolonging the reaction time (2 min in 30 min, 3 min in 60 min). The content of glycerol also plays a significant role in the side length of hexagonal nanosheets. A glycerol excess increased the formation of the crystal nucleus and, as a result, the Au nanosheets were smaller. Without glycerol, the Au phase cannot be formed under the same conditions.

The MW-assisted polyol process, involving glycerol, was exploited by Kou and Varma (2013)¹³ to fabricate Ag nanowires. They used sodium dodecylsulfate (SDS) to prevent Ag nanowires from becoming thicker. Bundles of Ag nanowires were obtained by reducing the amount of SDS, while unbundled Ag nanowires were formed when a SDS excess was used. The thickness of Ag nanowires was controlled by adjusting the amounts of glycerol and AgNO₃. Interestingly, Ag nanowires were obtained in 1 min and the diameter depended on the amounts of AgNO₃, glycerol, and SDS used. The Ag particles did not form at the same temperature when the reaction was carried out under conventional heating. The prepared Ag nanowires showed excellent catalytic activity in transforming 4-nitrophenol into 4-aminophenol and proved themselves to be much more reusable than Ag nanoparticles.

3. Ultrasound-assisted reactions in glycerol

The high acoustic impedance and viscosity of glycerol at room temperature suggest it would be best used with US irradiation over the 35-40 °C temperature range. Cravotto *et al.* (¹⁴) were the first to describe the application of both US and MW irradiation (stand-alone or combined techniques) to the carrying out of different types of organic transformations in glycerol: 1) the catalytic transfer hydrogenation of benzaldehyde to benzyl alcohol in which glycerol plays the dual role of the solvent and hydrogen donor (Scheme 10 A); 2) palladium-catalyzed Suzuki cross-coupling (Scheme 10 B); and (3) the Barbier reaction (Scheme 10 C). In all cases glycerol showed itself to be a

greener, less expensive and safer alternative to classic volatile organic solvents. Good yields were reported when non-conventional techniques, such as US and MW, were used. These techniques go some way to solving glycerol's problems of solubility and high viscosity by enhancing heat and mass transfer in all of these organic reactions.



Scheme 10 Benzaldehyde transfer hydrogenation (A); Suzuki cross-coupling (B); Barbier reaction.

4. Glycerol as a versatile building block

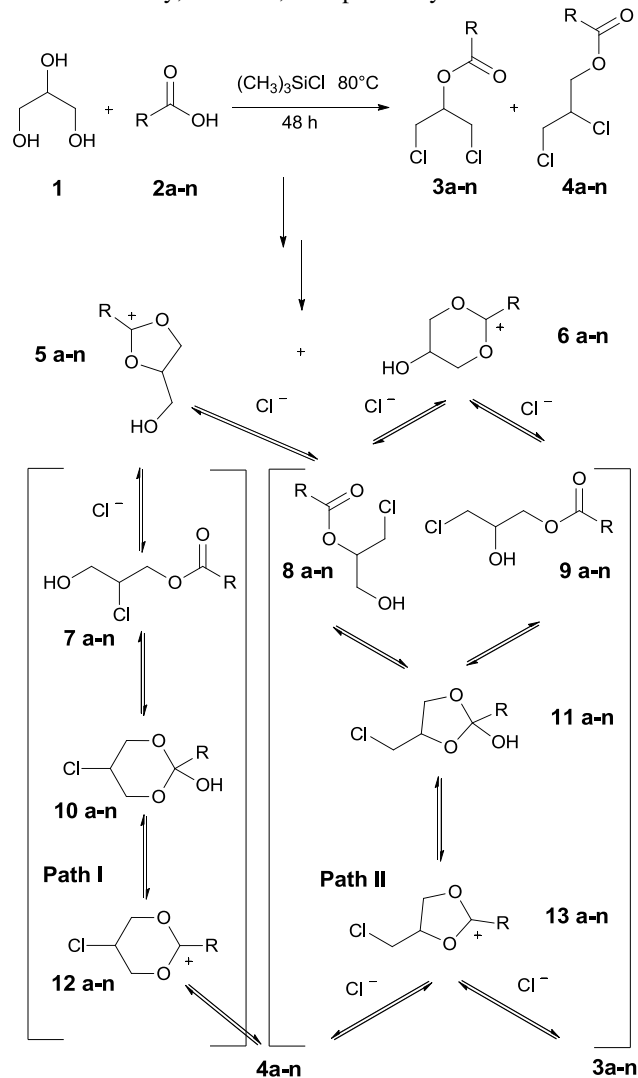
As reported in the literature, MW and US irradiation can enhance glycerol reactivity. The two main types of conversions are: catalytic modifications and bioconversion.

4.1 Catalytic conversion under MW irradiation

Chlorotrimethylsilane (CTMS) has been used as an acidic catalyst for a direct esterification-substitution of glycerol giving dichloropropyl esters (Escribà *et al.*).¹⁵ The authors reported that glycerol could be regioselectively transformed into 2-chloro-1-(chloromethyl)ethyl alkyl and aryl esters via a kinetically controlled process (Scheme 11), while avoiding solvent use and using either classical or MW heating. The proposed mechanism (using a ratio of reagents that is close to equivalence) entails glycerol transformation to the 2,3-dichlorohydrin regioisomer via the 4-4-chloromethyldioxolanic (pathway II) rather than the 5-chlorodioxolanic (pathway I), whatever heating system is used (Scheme 11).

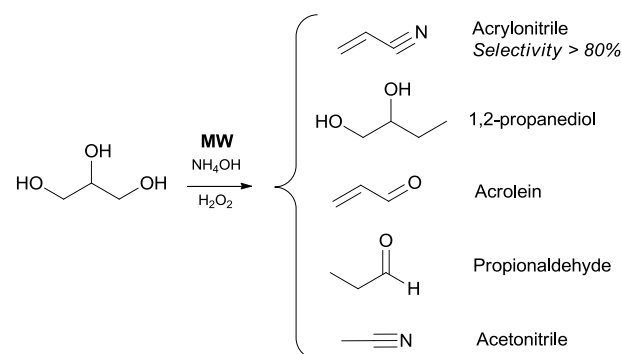
Kinetic control determined the regioisomer excess. Pathway II allows kinetic rather than thermodynamic control of the reaction, whereas pathway I opens a different path to the 2,3-regioisomer. MW reactor use may favour this pathway and, furthermore, MW irradiation at low temperature may bring together good reaction rates (52-73%) and kinetic control. A plausible mechanism was proposed on the basis of computational and experimental studies. The rearrangement process from 1,3- to 2,3-regioisomers may involve the nucleophilic attack of the sp² oxygen present on the carboxylic group which would form 1,3-dioxolane cations (Scheme 11 (13a-n)).

Another example of MW-assisted catalyzed conversions of glycerol can be found in the synthesis of acrylonitrile which is currently produced at high temperatures (400 °C) using propylene as a starting material, which is itself typically obtained by steam cracking or catalytic cracking of petroleum fractions. It may, however, be replaced by a renewable source;



Scheme 11 Simultaneous esterification and chlorination of glycerol using carboxylic acids, chloromethylsilane (CTMS) and chemical heating.

glycerol. Calvino-Casilda *et al.* in 2009¹⁶ described a novel cost-effective and solvent-free route to acrylonitrile from glycerol under MW-activation, thus presenting a selective new process for glycerol valorisation.

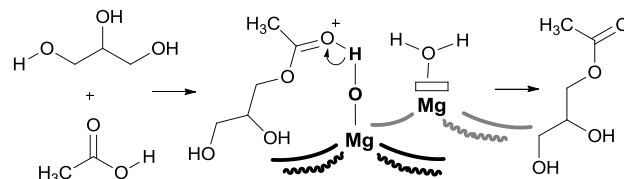


Scheme 12 Possible products in the catalytic reaction of glycerol with ammonia and hydrogen peroxide under microwave activation.

The liquid phase reaction of glycerol with ammonia and hydrogen peroxide was conducted using an alumina supported V-Sb-O as catalyst (Scheme 12). This process gave efficient solvent-free conversion (47%) of glycerol into acrylonitrile under mild conditions (100 °C) and short reaction times (1 h) (Scheme 12). In addition, MW-activation increased selectivity (> 80%) over conventional thermal activation (~ 60%). This reactive system is significantly more efficient than conventional gas-phase thermal activation which demands much higher temperatures to afford 58.3% selectivity to acrylonitrile at 82.6% glycerol conversion.

Castida *et al.*¹⁷ have also studied the niobium doping of SbnV/Al₂O₃ catalysts that may also be able to give acrylonitrile production from glycerol under MW. They confirmed that the main advantage of MW activation was the ability to quickly convert glycerol into acrolein, which is a reaction intermediate to acrylonitrile. They defined that binary, alumina-supported antimony-vanadium mixed oxide catalysts are efficient, with Sb1V/Al^{**} being the most active and selective towards acrylonitrile. Furthermore, it was found that the presence of the rutile VSbO₄ phase appears to be necessary to forming the C–N bond. The MW-assisted reaction of glycerol on this sample led to very satisfactory results, affording acrylonitrile selectivity close to 90% at conversion values near to 50%, whereas ternary systems involving niobium were deemed to be inefficient in the MW-activated conversion reaction of glycerol to acrylonitrile.

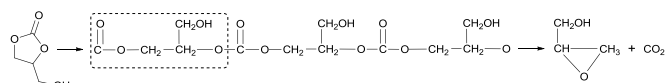
Some biodiesel additives that improve the fuel's solidification point and viscosity properties are glycerol-based derivatives, namely di- and triacyl glycerin, obtained via glycerol esterification with acetic acid. Troncea *et al.*¹⁸ have demonstrated that partly hydroxylated nanoscopic inorganic fluorides (MgF_{2-x}(OH)_x with x < 0.1) show good catalytic behaviour in the acylation of glycerol with acetic acid to acylated DAG (diacetylglycerine) and TAG (triacylglycerine) compounds (Scheme 13).



Scheme 13 An example of the acetylation mechanism involving a Bronsted/Lewis pair from the magnesium fluoride catalyst.

The use of glycerol-based additives to improve the properties of biodiesel or gasoline is one of the possible applications of this

renewable feedstock that are currently being explored. Catalytic activity depends on the density of acid sites at the external catalytic surface, while selectivity to various acylated products is influenced by the nature of the acid sites (Lewis and/or Brønsted). Optimal glycerol conversions (>90%) and selectivity to the desired compounds (over 85%) were obtained using non-conventional activation methods such as MW or US irradiation. In this way, the reaction time necessary to reach the same conversion level (>90%) can be shortened from 22 h (by conventional heating at 100 °C) to 4 h (by MW irradiation at 100 °C) or only 30 min (by US irradiation even at room temp.), using a molar stoichiometric acetic acid/glycerol ratio of 3/1. Presumably the non-conventional techniques, especially sonication, overcome the mass- and energy-transfer hurdles associated with these transformations. Glycerol carbonate is the most valuable intermediate in the production of glycidol, which is a polymerization precursor. In addition, glycidol is also used as a stabilizer for natural oils and vinyl polymers, as a demulsifier, in surface coatings and in the chemical synthesis of several intermediates, pharmaceuticals and as a gelation agent in solid propellants. Bolívar-Díaz *et al.* (),¹⁹ reported the use of MW and US irradiation to carry out the liquid-phase synthesis of glycidol from glycerol carbonate in solvent-free conditions (Scheme 14). A heterogeneous cost-effective, micro-ZnO supported Co₃O₄ nanoparticle catalyst was used under mild reaction conditions (150 °C) at atmospheric pressure. They reported the highest selectivity to glycidol from glycerol carbonate to date (>99%) at high conversion values (71%).



Scheme 14 Reaction mechanism for the synthesis of glycidol from glycerol carbonate.

This was a good alternative to conventional heating and classic catalysis as we search for new routes to transform glycerol and its derivatives into high added value chemicals while impacting less on the environment, which obviously results in a more efficient use of energy and materials (no solvent, heterogeneous catalyst and total selectivity).

Value can be added to glycerol by employing it in existing applications and at the same time finding novel ways to exploit it as a renewable fuel (H₂, syngas). Fernández *et al.* ()²⁰ have described a novel method for syngas (H₂ + CO) production (up to 81 vol.%) from the MW-assisted pyrolysis of glycerol over a carbonaceous catalyst; an activated carbon obtained from bituminous carbon (BC) and a carbon made from coconut shell (CC), both activated with steam. The influence of the heating method (electrical furnace and MW oven) and temperature (from 400 to 900 °C) on the pyrolysis of glycerol was also studied (Fig. 2). The main advantage of using a carbonaceous catalyst appears to be its higher selectivity toward hydrogen, resulting in a synthesis gas with a greater H₂/CO ratio especially under MW heating and even at low temperatures (400 °C). This proves that MW heating could be used to upgrade the industrial surplus generated from bio-diesel production.

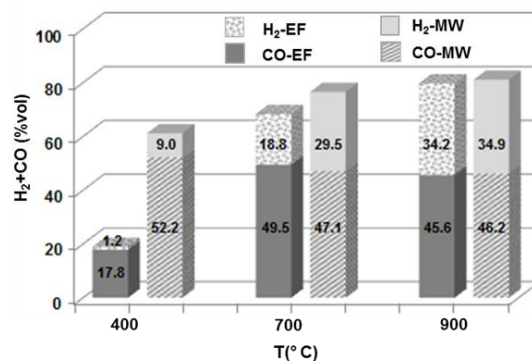


Fig. 2. Synthesis gas production (H₂ + CO) from the conventional (EF) and microwave (MW) pyrolysis of glycerol at different temperatures.

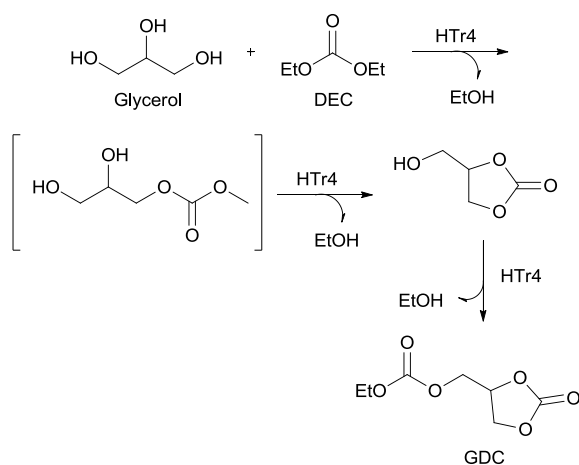
Moreover, they found that comparing different processes (pyrolysis, steam reforming and dry reforming) using activated charcoal as catalyst, the process that employed oxidizing agents (CO₂ or H₂O) gave a higher glycerol conversion.²¹ Steam reforming generates the lowest gas fraction and the highest amounts of hydrogen and syngas, while the opposite occurs in the dry reforming experiments.

Fernández *et al.* have demonstrated that MW processing promotes higher conversions of glycerol to gaseous products as well as higher H₂ and syngas yields compared to conventional heating even at low temperatures (400 °C). Moreover, the use of carbon-based catalysts appears to be highly suitable for producing synthesis gas with a H₂/CO ratio close to 1 while also keeping CO₂ emissions low.

4.2 Catalytic conversion of glycerol under US irradiation

Medium chain glycerides (MCG) have several applications in the food, pharmaceutical and cosmetics fields. Deshmane *et al.* ()²² have described a sonochemical procedure for the synthesis of an MCG that is based on the esterification of C₈-C₁₀ fatty acids and glycerol (catalyst conc. H₂SO₄ 5 wt% of fatty acid). Best conversion (98.5%) was obtained at 90 °C with a 1:3 fatty acid to glycerol molar ratio in 6 h using an US horn working at 22.5 kHz (240 W). They observed that the time needed to carry out the esterification reactions decreases from about 24 h (observed in traditional routes) to about 6 h. This is due, in particular, to the enhanced rate of mass transfer, the better mixing and local rise in the temperature that are generated by the US cavitation hot spots.

Another interesting example of glycerol catalytic conversion is the synthesis of glycerol carbonate. In this framework, Alvarez *et al.* (2010)²³ have described a transesterification reaction with DEC (diethyl carbonate) under US irradiation, (Scheme 15).



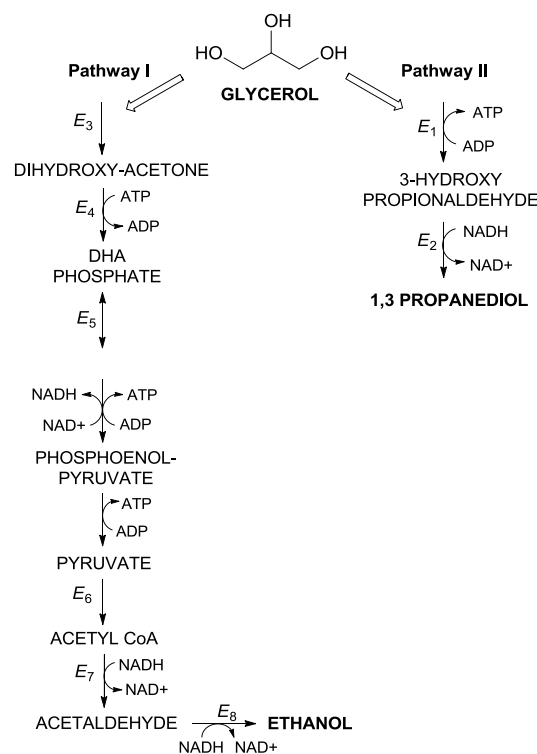
Scheme 15 Consecutive hydrotalcite-catalyzed transesterification reaction of glycerol with DEC.

This green, efficient and selective process was catalyzed by a number of hydrotalcite-like compounds, containing a Mg/Al molar ratio of 4, which were activated by calcination and followed by rehydration under US. The highest activity in terms of glycerol conversion was found in the US rehydrated hydrotalcite catalyst HTr4 (99% in 10h), which showed basic Brønsted sites and which can be reused several times without significant loss in activity.

A key topic in the catalytic conversion of glycerol is the combined use of US and enzymes. An example of the US-assisted enzymatic transesterification of glycerol for the production of 1-glycerol benzoate was reported by Ceni *et al.* ().²⁴ They described a promising technique which may help overcome the mass transfer limitations that come with the use of glycerol as a substrate. The cavitation energy accelerated the reaction rate, possibly by increasing the substrate's access to the active site, and a simple comparison of these results with those obtained earlier by Ceni *et al.* shows that similar and higher conversions were obtained here than with more classic organic solvents and pressurized fluids, respectively.

4.3 Bioconversion of glycerol under US irradiation

Microbial conversion of glycerol deserves a great deal of attention as it is cheaper, operates at ambient conditions and shows higher selectivity, thus making it more convenient and environmentally friendly than the catalytic route. The main drawback of glycerol bioconversion (as with all other fermentation processes) is the slow kinetics. A possible way to enhance such biochemical processes is the application of US. Khanna *et al.* ()²⁵ have investigated the US assisted bioconversion of glycerol by *Clostridium pasteurianum* to 1,3-propanediol (1,3-PDO) and ethanol (EtOH) (Scheme 16) from a mechanistic viewpoint. A dual approach of coupling experiments under US irradiation or mechanical shaking with simulations of cavitation bubble dynamics were described. It was found that US irradiation of the fermentation mixture enhances the yield of both glycerol bioconversion product and also displays some interesting trends with respect to the initial glycerol concentration.



Scheme 16 Metabolic pathways for glycerol bioconversion to ethanol and 1,3-propanediol. (Enzymes: E₁=Glycerol dehydratase; E₂=1,3-PDO dehydrogenase; E₃=Glycerol dehydrogenase Type I; E₄=Dihydroxyacetone kinase; E₅=Triose phosphate isomerase; E₆=Pyruvate dehydrogenase complex; E₇=Acetaldehyde dehydrogenase; E₈=Alcohol dehydrogenase).

Clearly, the role of US was purely physical in nature and had no influence on the basic biochemistry of the glycerol conversion. Moreover, due to substrate inhibition, the US enhancement effect was less marked with 1,3-PDO than with EtOH.

At a later stage Khanna *et al.* ()²⁶ carried out an in-depth examination of the mechanistic aspects of US based glycerol bioconversion enhancement with immobilized microbial cultures of *Clostridium Pasteurianum* on a silica support. They have observed that glycerol uptake by cells was not affected by either immobilization or US. However, both immobilization and ultrasonication are found to have a positive effect on glycerol consumption. This was found to be a function of initial glycerol concentration and was most marked at the highest glycerol concentration of 25 g/L. The immobilization of cells shifted the metabolic pathway almost completely towards 1,3-PDO. An analysis of enzyme kinetic parameters reveals that sonication of the fermentation mixture leads to increased substrate-enzyme affinity and decreased substrate inhibition for 1,3-PDO dehydrogenase which is then manifested in terms of the preferential conversion of glycerol into 1,3-PDO.

5. Conclusions

In summary, a significant increase in the applications of glycerol, ranging from the small lab to the full industrial scale, both as solvent and a building block is in progress. The main driving forces behind this, not-unexpected, success in chemical processes and synthesis are safety issues, easy storage, handling and disposal, low environmental impact and cost. The unique

physicochemical properties of glycerol enable fast dielectric heating and excellent acoustic cavitation under sonochemical conditions. Both energy sources are well suited to reactions in glycerol and to its conversion into other valuable fine chemicals.

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Notes and references

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