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https://doi.org/10.1016/j.rser.2020.110501

Glycerolysis of free fatty acids: a review

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Abstract

Lesser-polluting and carbon-efficient systems are the new standards of energy, globally. Biodiesel is an excellent bioenergy source due to its industrial feasibility and engine adaptability. However, biodiesel resource inventory still lacks feedstock flexibility on a commercial scale and mostly relies on vegetable oils for production. This creates a problem regarding allotment of resources for biodiesel production, at the cost of the food supply. An alternative is to consider the low-grade non-edible sources of oil, which contain high free fatty acids such as the crude vegetable oil refining rejects and waste cooking oil. To make it worst, the surplus crude glycerol glut is caused by the increased biodiesel production. Crude glycerol is refined for numerous other purposes such as for chemical synthesis. However, re-routing the crude glycerol in-situ for the pre-treatment of low-grade feedstock is suggested as one of the ways in increasing biodiesel profitability and sustainability. This review is focused on the use of glycerolysis reaction as a method of reducing free fatty acids content. A broad spectrum of different catalysts such as enzymatic, homogeneous and heterogeneous, as well as hybrid systems, was reviewed and discussed. Based on the findings, suggestions regarding the development of the glycerolysis reaction were made. In comparison to the homogeneous catalyst, more yield at the increased residence time is obtained for the heterogeneous catalyst. However, leaching, thermal degradation and swelling are the known problems of the heterogeneous catalysts, while product separation is a challenge with homogeneous catalysts. Development of homogenous-based catalysts is suggested as a focus for future studies in glycerolysis reactions.

Highlights

- Glycerolysis to improve quality of low-grade feedstock is reviewed.
- In-situ crude glycerol valorisation to increase biodiesel profitability.
- Advance process intensification techniques provide better mass-transfer.
- Homogenous catalysts based glycerolysis give better FFA conversion profile.
- Homogenous catalyst gives low monoglycerides selectivity.

Keywords: Catalyst; Biodiesel; Esterification; Free fatty acids; Glycerol; Glycerolysis

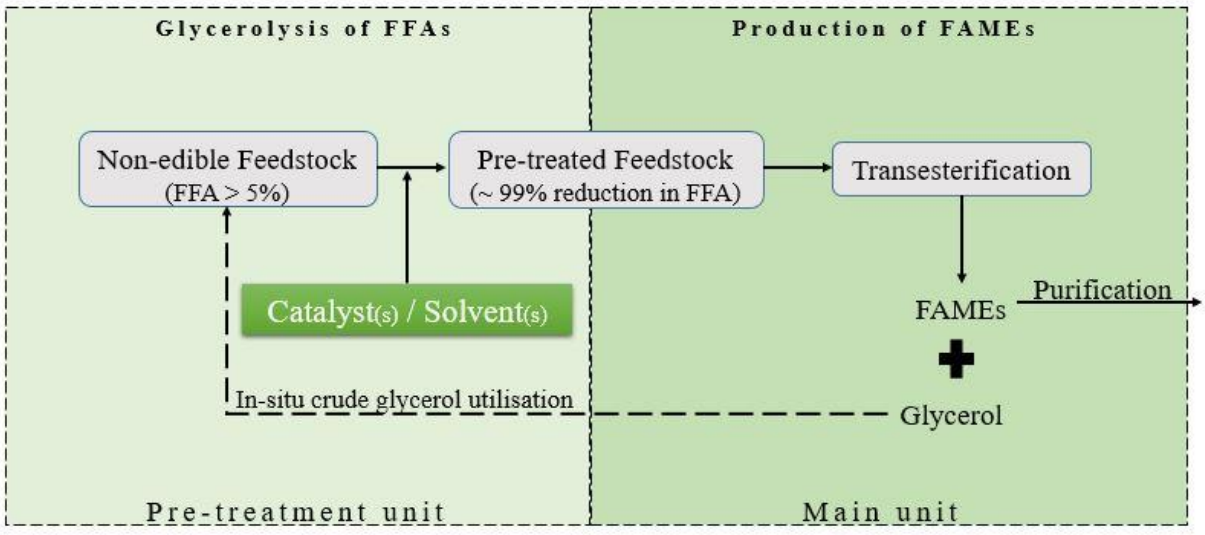
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List of abbreviations

Amberlyst	Trade name of a range of sulfonic acid ion exchange resins with suffix as -15, -16, and -31, representing different types.
ATPB	Allyl triphenylphosphonium bromide
PTSA	Para toluene sulfonic acid (PTSA)
DAG	Diacylglycerol/glyceride
DES	Deep eutectic solvents
DG	Diglyceride
DMC	Dimethyl carbonate
E_{act}	Activation energy
FFA	Free fatty acid
FAAE	Fatty acid alkyl esters
FAME	Fatty acid methyl esters
GC	Glycerol carbonate
Gly	Glycerol
HHV	High heating value
KOH	Potassium Hydroxide
MAG	Monoacylglycerol/glyceride
MG	Monoglyceride
NaOH	Sodium Hydroxide
N_2	Nitrogen
SBA-15	Santa Barbara Amorphous-15
SC-CO_2	supercritical carbon dioxide
TAG	Triacylglycerol/glyceride
TG	Triglyceride
UCO	Used cooking oil
WtE	Waste to energy

Graphical abstract



Contents

Abstract 1
List of abbreviations 2
Graphical abstract 2
1 Introduction 3
1.1 Alternative feedstock and associated challenges 4
1.2 Crude glycerol applications 6
2 Glycerolysis 9
2.1 Reaction mechanism 9
2.2 Parameters affecting glycerolysis 11
2.2.1 Temperature 11
2.2.2 Reactor type 11
2.2.3 Molar ratio 12
2.2.4 Solvent 13
2.2.5 Agitation unit 15
2.2.6 Glycerol purity 16
2.2.7 Catalyst type 18
2.3 Problems associated with glycerolysis 19
3 Catalysis 19
3.1 Enzymatic catalysis 20
3.2 Heterogeneous catalysis 24
3.3 Homogenous catalysis 30
3.4 Other catalytic systems 35
4 Conclusion and future trends 38
5 Acknowledgement 39
References 40

1 Introduction

The development of modern civilisation has laid tremendous stress on the earth by utilising prehistoric fossil deposits for energy [1]. Recently, the need for a steady transition to alternative energy systems has been triggered by climate change and energy security. The global energy demand is expected to reach 10^3 Exajoules or more by the end of 2050 if the current economic growth continues [2]. However, in contrast to renewable fuels, fossil fuels are more energy-intensive, hold the major share of capital, infrastructure and investments, globally [3]. Therefore, the question is: Can the new alternative energy systems co-exist with an established crude oil market, competitively?

The transportation sector consumes a great share of fossil fuels and more than three-quarters of automotive users are diesel-fuelled [4]. To replace this fossil fuel dependency, biodiesel has been researched intensively and still is a priority research area [5]. In addition to being

renewable, biodegradable and less polluting, biodiesel is essentially similar to that of diesel, so that it can fuel existing diesel-engines with minor modifications, if required [6].

1.1 Alternative feedstock and associated challenges

Currently, most of the biodiesel production uses edible oils from palm, sunflower, canola, soybean and corn [7-10]. The major drawback of using the edible feedstock is that the prices for these oil yielding crops have been increasing over past decades and these make up an important part of human diet [11]. In addition, when there is a consistent demand for feedstock for biodiesel production, change in land usage pattern is observed, this indirectly depreciates the carbon footprint of biodiesel [12, 13]. Since 2000, there has been significant growth in palm oil production, which is the highest oil yielding crop among major oil crops such as soybean, sunflower and rapeseed [14]. This has resulted in the exploitation of agricultural and forest land, by converting them solely for these oil crops [15]. Globally, prices for these vegetable oils are influenced by various factors such as weather and competition within producing countries; thus, are volatile [16]. To avoid such drawbacks, biodiesel production via dominant non-edible feedstocks as listed in Table 1, among other non-edible feedstocks has been investigated [17-20].

Table 1
Studies reporting biodiesel production from non-edible feedstock and their FFAs content.

S.no	Feedstock	FFA %	Ref.
1	Jatropha	0.18–77.5	[21-23]
2	Animal fats	5-30	[24]
3	Inedible tallow	2-5	[25]
4	Vegetable oil soap-stock & Vegetable oil deodorizer distillates	30-95	[26-28]
5	Yellow greases	<15	[29, 30]
6	Brown (or trap) grease	>15	
7	Microalgae	<15	[31-36]
8	Waste cooking oil	2-7	[37-39]

Following Kinast [40], the feedstock can be divided into four classes on the basis of FFA content: 1) refined oil (FFA <1.5%); 2) low FFA (FFA <4%); 3) medium FFA (FFA 4-20%) and 4) high FFA (FFA ≥20%). For biodiesel production, waste cooking oils has been one of the most tested feedstock while other wastes or side-streams of oil processing industry were used in lesser quantities [41]. When these low grade oils are used for biodiesel production, difficulties arise owing to high FFAs content, water and other impurities. [42]. Extensive technical reviews [43-46] and research reports [47] are available on biodiesel production from low-grade non-edible feedstocks. Usage of these non-edible lower quality feedstocks such as used cooking oil (UCO), has seen steady growth in the past decade, as per a report published by Union for the Promotion of Oil and Protein Plants (UFOP), as shown in Fig. 1.

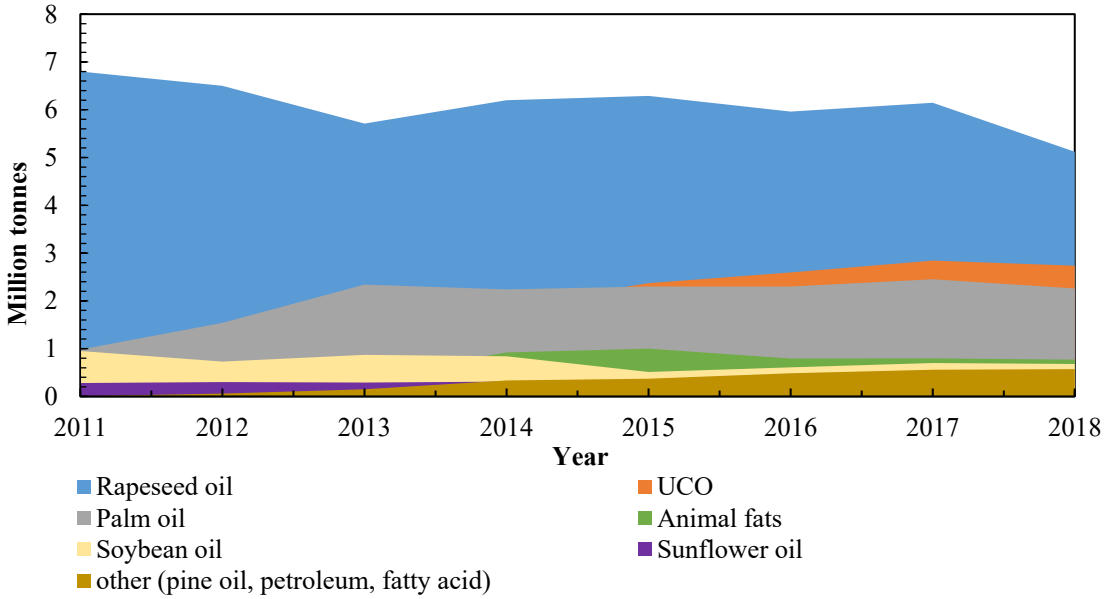


Fig. 1. Feedstock consumption trend in the European Union (EU) for biodiesel and hydrotreated vegetable oil production [48].

FAME mass conversion diminishes with increasing FFA content, as shown in Fig. 2. Degraded sunflower oil catalysed by KOH [49] and WCO catalysed by NaOH [50] are studied for the influence of the FFA content in the feedstock, on biodiesel production. It is seen that homogeneous base-catalysed transesterification, which is an established technology for biodiesel production, is sensitive to feedstock-purity. One reason for such sensitivity is the occurrence of the saponification side reaction between FFAs and the base catalyst [51]. Consequently, a required limit for initial FFA content is set to < 0.5% [52]. To reduce the FFA content in the low-grade biodiesel feedstock, three alternate pathways reported in the literature are:

1. Neutralisation with an alkaline catalyst [11],
2. Direct Acid-catalysed transesterification for converting FFA into biodiesel [53].
3. Esterification of free fatty acids [54].

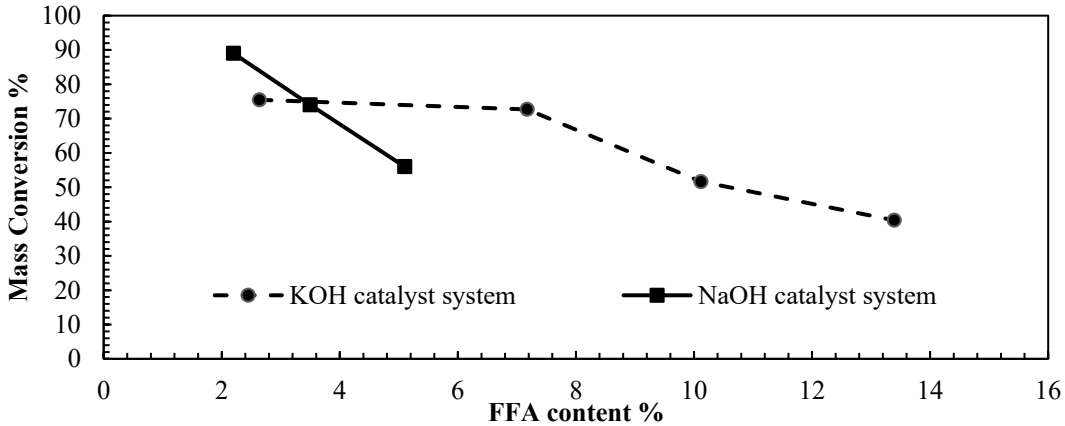


Fig. 2. Effect of initial FFA percentage on the FAME mass conversion. WCO is preheated and filtered at 70°C for 30 minutes.
Reaction conditions: 5:1 methanol to oil molar ratio, NaOH 0.01 wt%, 60°C for 2 hours [50].
1:5 mass ratio of methanol to oil, T = 65°C, t = 45 min, 0.5 wt% KOH[49].

However, these pathways have their individual problems. In the case of neutralisation and direct acid transesterification, no pre-treatment unit is used, and low-grade feedstock is introduced in the transesterification unit directly. As a result, in the case of the alkaline neutralisation, a certain amount of catalyst is used up in neutralizing the free fatty acids resulting in soaps; this additional amount is calculated using titration [51]. It also results in a reduction in the ester content as neutral oils are also lost by saponification [52, 55]. Saponification also negatively affects the washing units downstream because of the product emulsification, resulting in product loss [56-58].

On the other hand, in acid transesterification, longer reaction times, higher reaction temperature and corrosion problems render its use [59]. Also, the water produced from the reaction stops the reaction usually well before reaching the completion by inhibiting the acid catalysis [60]. To overcome the above limitations a single-pot combination of acid esterification, as pre-treatment of FFAs, followed by alkali transesterification of triglycerides is also possible[53]. To counteract the hindrance caused by water produced during acid esterification of FFAs, high molar ratios of alcohol (up to 40 moles CH_3OH per mole of oil) is added, so that water does not limit the reaction[53]. This in turn requires more energy to recover this excess alcohol. One thorough review of the biodiesel production via acid catalysis is done by Lotero, et al. [61].

Esterification of FFAs is a pre-treatment step to improve the feedstock quality. In the esterification, methanol is used owing to its lower cost and high reactivity [62]. Here also, higher molar ratios of methanol to oil (20-40) are required with acid catalysts such as sulphuric acid in a reaction [24]. Thus this also carries similar problems discussed above. Another route for esterification is using glycerol as the esterifying alcohol moiety; the reaction is commonly named as glycerolysis [63].

The biodiesel industry needs to find some solutions for commercial space competition with a conventional fuel dominated market. There are significant economic and environmental differences between the two fuels, especially in raw material procurement. The technology for crude oil exploration, in the case of fossil fuel, has been improving continuously and is extensively adopted during the past century [64, 65]. In the case of biodiesel, the production phase is comprehensive and consumes approximately three-quarters of total energy and resources [66, 67]. Its direct effect can be seen in the price difference between diesel and biodiesel. As of July 2019, The United States Department of Energy reported that across the US, the average retail cost for every gallon of 100% Biodiesel was USD 0.60 higher than that of fossil diesel fuel on a national average [68], even when biodiesel price is inclusive of the government subsidies [69].

1.2 Crude glycerol applications

Another point of consideration in the biodiesel industry is its bulk production of crude glycerol, which has flooded the market globally and opened up new research scopes for better utilisation of this by-product [70, 71]. For every ton of biodiesel produced, 100 kg of crude glycerol is produced [72].

Pure glycerol found in the market is refined and contains less than 5% impurities, which is not the case with crude glycerol obtained from biodiesel production. Crude glycerol is produced via either oil saponification (16% impurities), hydrolysis (10-12% impurities) or

transesterification (25-30% impurities) [73, 74]. Many other grades of glycerol are commercially produced such as United States Pharmacopeia (USP) standardised glycerine (<99% pure), methylated (10-20% methanol) and demethylated (<1% methanol) glycerol [75]. Apart from the impurities, one difference between these grades is the variations in higher heating value HHV (MJ/Kg), which 16.0, 21.8 and 20.8 in the order mentioned respectively [75].

The magnitude of glycerol market was over 2 billion USD in the year 2017 and its consumption was estimated to increase at a compounded annual growth rate of over 5% to $4x10^6$ tons by the year 2024 [76]. The biodiesel industry is growing and with it, the derived crude glycerol market. Crude glycerol market is forecasted to exceed USD 3.5 billion by the year 2024.

There is a wide range of applications for glycerol in the food, pharmaceutical, and cosmetic industries. A more elaborate insight into the global glycerol market is shown in Fig. 3. As of 2011, the crude glycerol production has spiked and the refined glycerol production has consistently decreased [72], showing that refining of crude glycerol is dominant in comparison to production through hydrolysis of fats or oils.

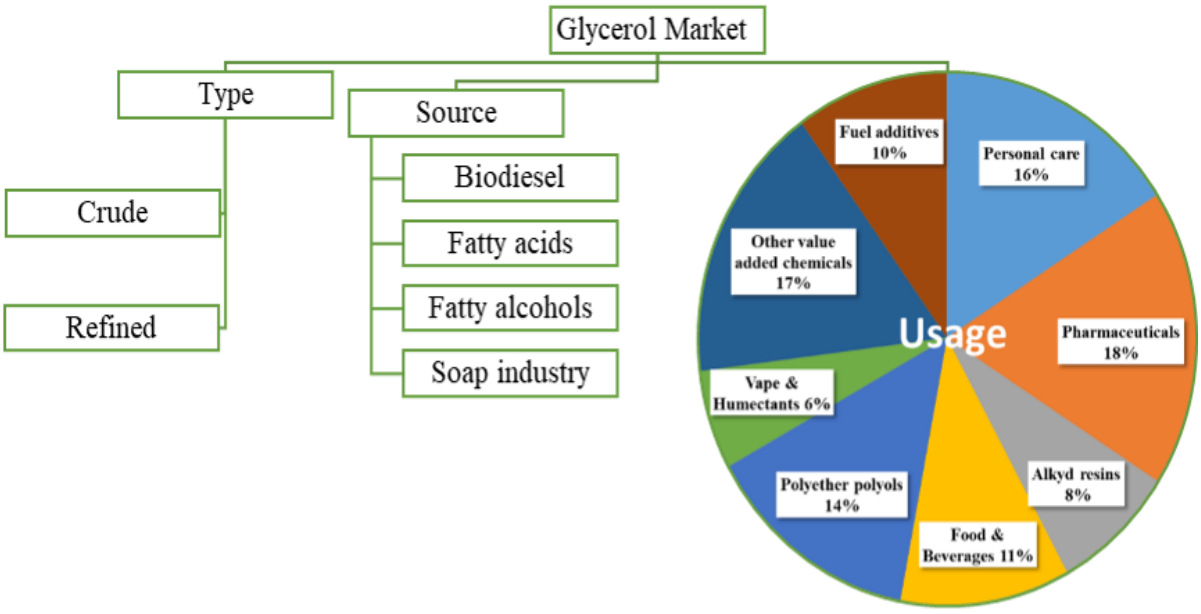


Fig. 3. Glycerol market flow chart, assisted with a pie chart showing percentage share of different applications. Data adapted from [59, 77].

However, this consumer-related industry is highly sensitive to the quality and source of glycerol production. Crude glycerol carries up to 30% of impurities in the form of glycerides, alcohol, water and salts of an alkaline catalyst, which are used in the transesterification process [78]. Thus, biodiesel derived crude glycerol has lesser applicability in these fields because of its impurities [79]. Also, the averages prices of 80% pure crude glycerol and 95% pure refined glycerol are $300/ton and $800/ton, respectively; implying the significant impact of its price on any process [80, 81]. Instead of refining the crude glycerol, other applications where the inferior quality of glycerol can be adopted is also an option. For example, the in-situ consumption of crude glycerol in the same biodiesel facility might be looked into. In this regard, applying glycerol for the production of fuel additives is one way of utilising the by-product, which may be more appropriate if done onsite [82, 83]. Investigations into the

production of mono-, di- and tri-tertiary butyl ethers of glycerol were investigated using heterogeneous catalysts [81, 84]. Production of triacetin using glycerol and acetic acid is also reported in the literature [85].

A glycerol based catalyst development was reported by Devi et al. [86]. They studied the carbonisation and sulphonation of crude glycerol to use it as an acidic catalyst for esterification of palmitic acid. However, high temperatures (180 °C), water washing and 1:4 w/w glycerol to sulphuric acid were used to synthesise this catalyst, making the whole scheme more energy-intensive. An alternative way of crude glycerol consumption is its combustion, a potential secondary on-site energy source. Bohon et al. [75] experimented with methylated and demethylated glycerol combustion in a laboratory custom made refractory burner. They reported a range of emissions from combustion and concluded that a high rate of emissions, especially oxides of nitrogen (NO_x) raises serious issues with crude glycerol combustion. Thus, making it not suitable for burning.

Crude glycerol production from biodiesel can also be avoided by selecting glycerol-free biodiesel production route. One such possibility is by adopting enzyme-catalysed transesterification, Novozym 435 is one such commercially available lipase having potential in bio-catalysed biodiesel production [87]. Similarly, instead of alcohol, DMC is used in bulk for transesterification of corn oil with Novozym 435 to produce FAMEs and glycerol carbonate [88]. However, the higher cost of lipases and its inhibition by alcohol, render them less attractive [89-91]. One comprehensive review in glycerol market demand and supply analysis was done by Ayoub et al. [70]. In this study, investigators systematically addressed various aspects of the modern glycerol market. Similarly, Anitha et al. [92] reviewed the glycerol market and possible application fields for glycerol utilisation. Region-wise crude glycerol production, market supply drivers and inversely proportional relation between crude glycerol price and its biodiesel-based generation have been very effectively displayed in their study. However, this study does not takes in-situ crude glycerol consumption as a possible usage scenario.

On considering the various aspects reviewed above sections, high FFAs containing feedstocks need to be explored for expanding biodiesel production. Also, the crude glycerol remains oversupplied in the market, given its production is directly proportional to biodiesel production. Thus, in this review, the primary consideration is on the glycerolysis as the pre-treatment of fatty acids in the biodiesel production. This has been one of the growing research areas in the last decade in crude glycerol incentivisation. In a recent study, animal fats (FFA>90%) after high temperature $ZnSO_4$-catalysed glycerolysis, were efficiently blended (up to 10%) with diesel and satisfied current blended fuel standards [93]. Since Sonntag's [63] critical commentary on glycerolysis of fats and esters, other reviews [94, 95] have examined glycerolysis from a food-industry perspective, due to heavy usage of glycerides as emulsifiers and additives. In this review, systematic reporting and comprehensive study of all the methods and techniques in reducing the FFA content of these non-edible feedstocks through the process of glycerolysis was undertaken. Glycerolysis of FFAs is studied from the viewpoint of usage solely in the biodiesel production. To the best of the authors' knowledge, to date no similar review has been made in the available literature, which explains the potential of this work for furthering the research in the area of sustainable biodiesel production from the highly acidic feedstock.

2 Glycerolysis

The glycerolysis reaction is used to convert free fatty acids into respective mono, di and tri acyl glycerol by esterifying them with the hydroxyl groups present in the parent oil or in the glycerol [96]. From this perspective, it is the esterification process in which glycerol acts as the alcohol to convert FFAs into the respective glycerides. Water is produced as a by-product. It is usually applied when FFA content is higher than 5% [97].

2.1 Reaction mechanism

The reaction between FFAs and glycerol is an alternative to conventional esterification pre-treatment to bring down FFA content (acid value < 1 mg KOH/g) [98] so that base-catalysed transesterification can occur along the process chain. A typical simplified glycerolysis reaction scheme is shown in Fig. 4. Glycerol has three hydroxyl groups attached to it and it is a hydrophilic molecule and hence it is decidedly less soluble in organic solutions; for example, it is only 4-5% soluble in common fats which are hydrophobic themselves [63]. This low solubility hinders the reaction and unless the reaction is carried out with a catalyst, it takes a longer reaction time at higher temperatures around 250°C, where glycerol solubility is approximately 45% [63]. This limit is owing to the pyrolytic instability of fats which is due to thermal sensitive double bonds in the carbon chain [99]. The saturation position in the carbon chain affects the reaction rate by reducing it considerably if the double bond is adjacent to the carboxylic group in olefinic acids, as expected from the electronic theory of organic chemistry [100]. In this continuous reaction scheme, FFAs react with glycerol producing MGs and from there the reactants further esterified into DGs and TGs [101]. Thus, at any moment all the three glycerides are present in the product. The by-product water produced is neither absorbed nor eliminated and must be removed by either nitrogen purging, or other methods, to keep the reaction in the desired forward direction [63].

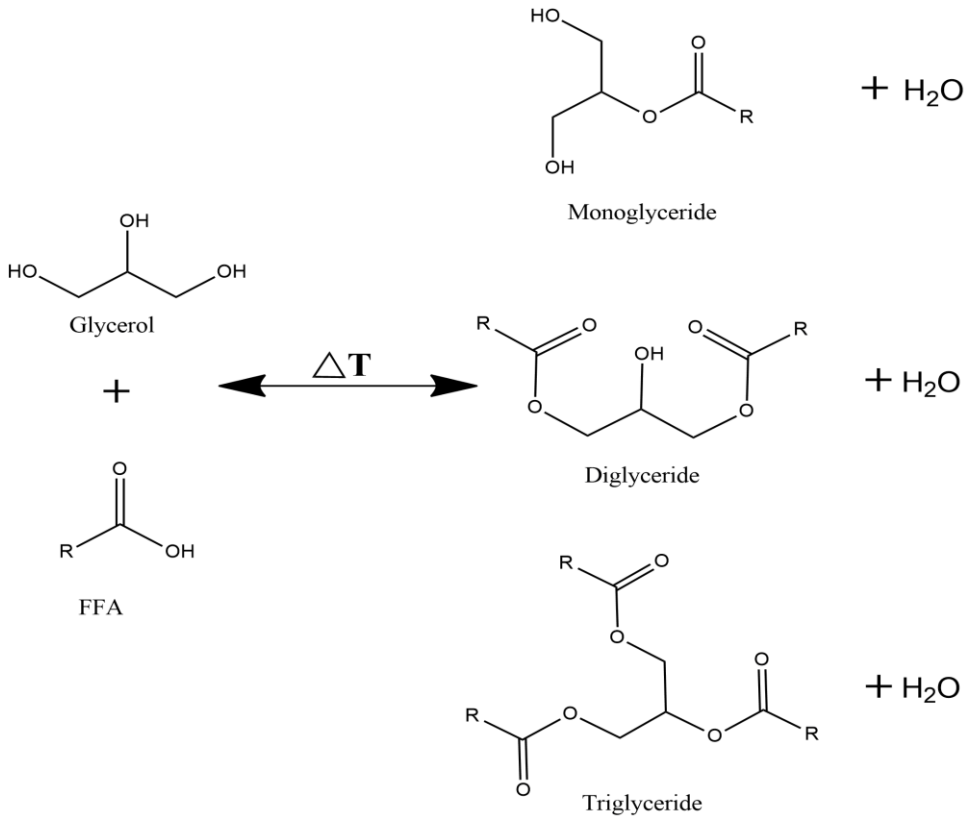


Fig. 4. Reaction scheme for the high-temperature glycerolysis of FFAs, adapted from [97, 102].

Of the total monoglycerides produced through glycerolysis, 2-acyl or beta-monoglycerides form frequently at every temperature, being 5-8 % at lower temperatures and around 30% at very high temperatures [63]. When carried out under adequate homogeneity, glycerolysis is a reversible reaction and thus subjected to the Mass Action law [63]. Conventionally, an excess of glycerol is required to push the reaction forward. Typically, towards near completion in a high-temperature glycerolysis reaction, this excess glycerol is usually removed. However, following the Mass Action law, the reaction shall reverse itself towards the formation of more glycerol. Hence the reaction mixture is cooled to room temperature or even below to ensure that no reverse reaction takes place, owing to the low miscibility of reactants at lower temperatures [103]. Overall, glycerolysis is a straightforward reaction involving two reactants stirred at high temperatures, yet it is one of the most complicated reactions in oleo chemistry.

For the kinetics of glycerolysis of oleic acid, the second-order rate kinetic is mostly reported in the literature [53, 62, 69]. For reactions at high temperatures (230°C), Tu et al. [104], reported first-order reaction kinetics with a rate constant -1.4245 hr^{-1} and activation energy of 69.14 kJ/mol. In the later phases of the reaction, there is a decrease in MAGs concentration due to conversion of MAGs to DAGs which later on react with FFAs to form TAGs [104]. The reaction is fundamentally bimolecular and, when studied for glycerolysis of peanut oil fatty acids, the rate constant in the early phase of the un-catalysed reaction is substantially higher than near the completion phase [105]. The change in the MAGs concentration at the early and final phases of the reaction might be a reason behind such difference in rate constants. Also, the glycerol solubility is inversely proportional to TAG content, percentage of which increases at final stages of the reaction [106]. An effort in continuous extraction or separation of MAGs from the reaction mixture can possibly keep the reaction at higher rate constants, thereby enhancing the MAGs yield.

2.2 *Parameters affecting glycerolysis*

2.2.1 *Temperature*

As previously discussed, to prevent oil degradation, the upper limit of temperature is around 250°C. The reaction is also blanketed from external agents, as air interactions above 200°C increase the acidity and peroxide value of the reaction system [63]. This increased acidity in the reaction may cause glycerol conversion to acrolein, which is very toxic, at the upper limits of temperature, though normally not in the case of alkaline catalysts [107, 108]. Hence, nitrogen purging is employed to alleviate these problems and sweep out the water molecules formed in the reaction. However, vacuum distillation and silica gel are also other options [49]. Prominent variation in glycerolysis was observed between 180 to 220°C, as shown in Fig. 5. The increase in the homogenisation due to the increase in temperature is the reason behind this enhancement [97]. At temperatures beyond 220 °C, a slight increase in the selectivity of diglycerides and triglycerides is observed, shown in Fig. 1. Other investigators reported similar trends with, Mićić et al. (81% conversion) [49] and Blanco et al. (90% conversion) [109] achieving the highest conversion of FFAs at 220°C and consequently reported that both FFA conversion and MG selectivity in the product, slightly decreased and then stabilised beyond this temperature, respectively. No reasoning behind such trend is provided by the authors. This may be because of the increased rate constants for the glycerolysis reaction, which in turn affected MG to DG to TG conversions in near completion stages of the reaction. Since, the glycerol solubility is inversely proportional to triglyceride content, with slight increase in TG selectivity in the product, this may have further caused slight decrease in FFAs conversion.

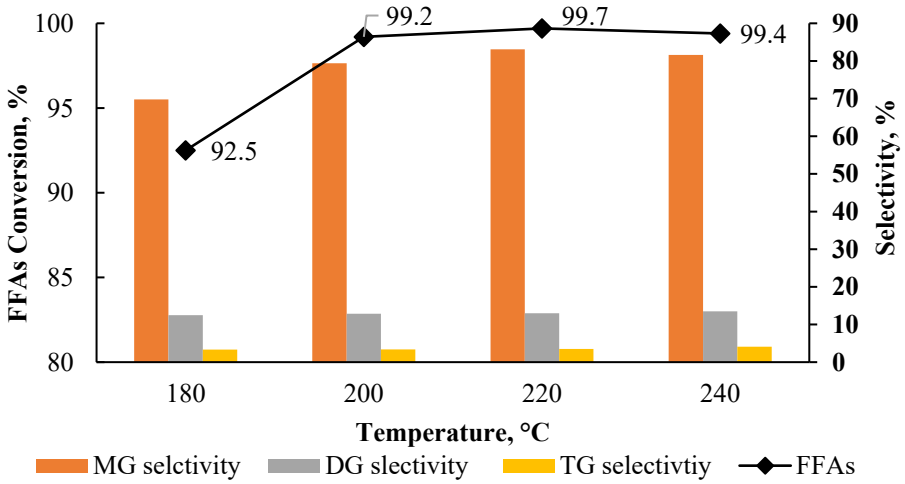


Fig. 5. Effect of temperature on the FFAs conversion and MG, DG and TG selectivity in a non-catalysed glycerolysis. Oleic acid to Glycerol- 1:6, 600 rpm. Data adapted from [110].

2.2.2 *Reactor type*

A batch reactor is most commonly used in the glycerolysis reaction [63, 111]. The rationale behind it being typically the discontinuous supply of non-edible feedstock and non-uniformity in the feedstock characteristics. In such scenario, a batch reactor is the most economic and able to handle the adjustments needed for varying characteristics of discontinuous feedstock supply [112]. Islam et al. [106] studied the laboratory-scale batch reactor using Artificial Neural Network, to study the reaction kinetics of glycerolysis of palm fatty acid distillate, carried out

in an open reactor system with N_2 purging and feeding 4% excess of glycerol. They reported over 98% reduction from the initial acid value (85 mg KOH/ g) in 90 minutes at 200°C. Effective water removal via N_2 purging, showed strong dependency with the reaction rate, by increasing molecular collisions.

However, modern researchers have also experimented with continuous micro-reactors [113]. In another study, a single bubble cap tray-continuous stirred tank reactor was studied by Negi et al. [114]. Higher ester conversion (98%) but lower MG selectivity (40%) were reported in the base-catalysed glycerolysis of fatty acid methyl esters (FAMEs) carried out at 143°C under atmospheric pressure with a residence time of 85 minutes and gas velocity of 1.6 m/s. While for continuous stirred tank reactor (CSTR) with a residence time of 100 minutes, operating at 140 °C, 500 rpm and 0.3 bar, the ester conversion and MG selectivity were, 65% and 36%, respectively. In comparison to the aforementioned two types of reactors, in case of the batch reactor operated at 135°C under atmospheric pressure, the ester conversion and MG selectivity was 98% and 48% in 125 minutes, respectively. N_2 purging was applied for methanol stripping in both CSTR and batch reactor. In the bubble reactor setup, when equal volumes of the liquid hold-up were used with multiple cascaded trays instead of a continuous tray, there was a drop in conversion. The reason is that even in a single bubble cap tray reactor, the inferior initial mixing regime was seen, evident from the reaction kinetic studies. So, for multiple cascading, the mixing regime deteriorated further. Hence, such reasons imply that the bubble cap tray reactor brought no further improvement over stirred tank reactors. Continuous reactor-based investigations, for the glycerolysis of FFAs, has not been reported so far in the literature. However, such an investigation is important to verify the results reported in glycerolysis of FAMEs, in the case of glycerolysis of FFAs. Similarly, there hasn`t been any investigations on the use of the continuous microreactors in glycerolysis of FFAs. However, at the present, the batch reactors are the most preferred types of reactors.

2.2.3 Molar ratio

As it is already established, the reaction is reversible in nature and hence an excess of glycerol is required. Since the reaction takes place in the FFA phase and not in glycerol phase, there will be an upper limit to concentration for glycerol in FFA phase where the reaction takes place and beyond this concentration will not be actively participating and will just increase glycerol phase volume. The effect of the molar ratio of oil to glycerol on the reaction kinetics and conversion rate has been well researched and reported in the literature. Initially, the investigators only reported constant molar ratios in their studies, such as equimolar, equivalent mass [115, 116] or specified molar ratios [117]

A molar ratio of 6:1 glycerol to oil at 220°C and 300 kPa is reported as the optimum condition when the waste cooking oil was used as a feedstock [49]. The ratio of 6:1 glycerol to oil is in line with similar glycerolysis studies [97, 110]. The excess of glycerol past this ratio usually has no appreciable effect on conversion [110], as shown in Fig. 6, (a). This behaviour may be understood from the perspectives of excess and limiting reagents in any reaction [118, 119] i.e. the excess of one of the reactant can push the reaction forward to a certain extent only. The yield of the monoglycerides also follows the same trends as that of oleic acid conversion, showing the correlation between these two in the non-catalyzed glycerolysis whereas, for the diglycerides and triglycerides, it follows inversely as shown in Fig. 6, (b).

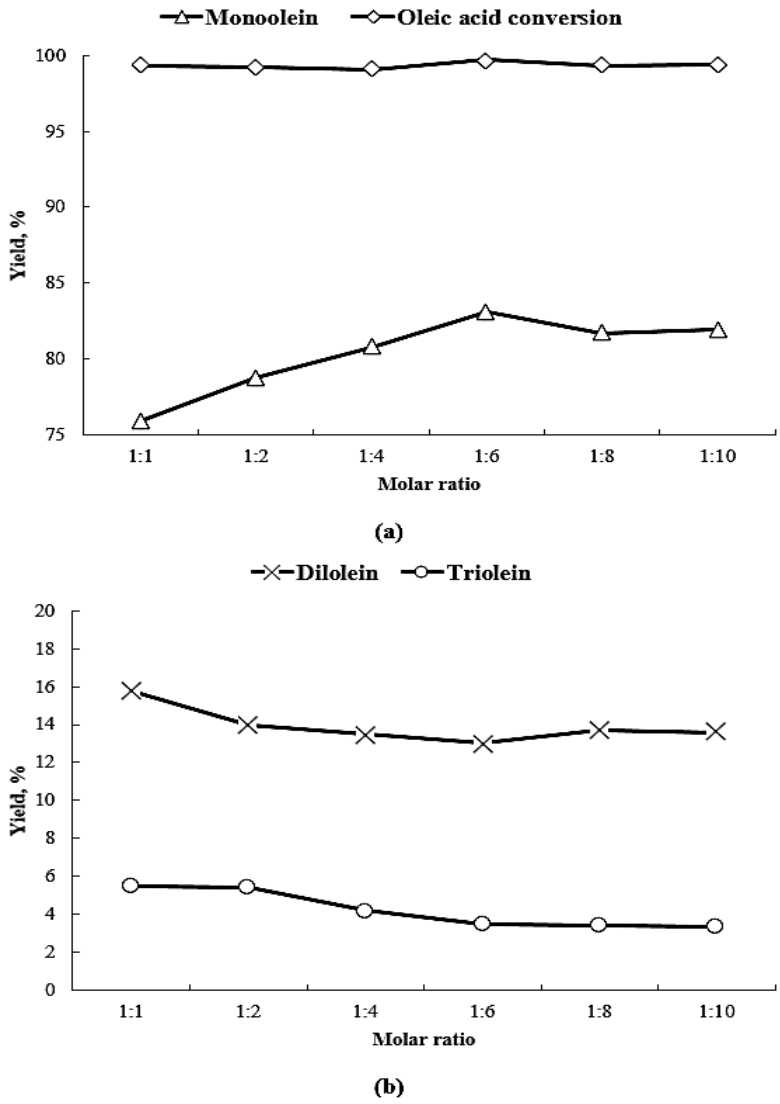


Fig. 6. Effect of oleic acid to glycerol molar ratio on; a) oleic acid conversion and monoolein yield and b) diolein and triolein yield in the product. Data adapted from [110]. Reaction conditions- 220°C, 600rpm, 300-minute reaction time, 80ml/min N_2 purging.

2.2.4 Solvent

The solubility of glycerol in different kinds of free fatty acids is shown in Fig. 7. Apart from caprylic and capric acid, glycerol is not much soluble in other FFAs. Furthermore, the percentage esterified in glycerolysis reaction at 180°C, follows a similar trend, i.e. caprylic acid being the most while stearic acid being the least converted, in the equivalent mix of FFAs with glycerol [116]. This implies that the solubility has significant effects in the glycerolysis reaction.

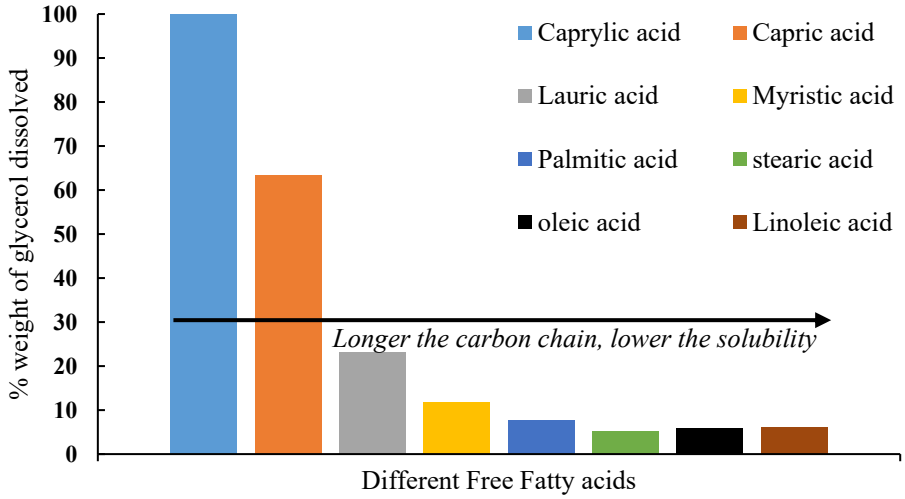


Fig. 7. Solubility of glycerol in different FFAs at 180°C. Data adapted from [116].

In the glycerolysis reaction, performed at higher temperatures (180-300°C) and using water under pressure (1-27 bar) as a solvent, a monophasic system is obtained [120]. This application of water under pressure, in addition to increasing the solubility of glycerol in the oil phase and monoglycerides selectivity, also avoids the formation of acrolein at 280°C [121]. However, the reaction higher input costs are associated with the described temperature and pressure; in comparison to the main transesterification reaction which works at rather mild conditions. A solvent or co-solvent may be employed in a catalysed reaction to facilitate the miscibility [122].

One fundamental study in this field was reported by Hartman et al. [116] in 1966. They investigated the esterification of glycerol with eight free fatty acids having different saturation levels. Equimolar/ Equivalent amounts of glycerol and acids were subjected to 180°C in solvent dowtherm A. Tert-butanol, dimethylformamide, monoolein, diglyme and dimethyl sulfoxide were some of the solvents in which high quantities of oleic acid and glycerol were found soluble [115]. Other solvents such as hexane, pyridine, phenol, toluene, o-cresol and quinolone have been studied in the glycerolysis reaction [116, 123-125]. At lower temperatures, the effect of solvents such as toluene, dimethylformamide, diglyme and dowtherm A, on the free fatty acid conversion was negligible, showing inhibition of thermal reaction at the same temperature, owing to modification of reactants surface properties. With a reaction time of 16 hours at 110°C and equimolar concentration of stearic acid to glycerol; toluene, dimethylformamide and diglyme gave 6%, 5.5% and 7.5% of FFA conversion, respectively whereas without solvent 30% of FFA conversion was achieved [126]. Similarly, the influence of tert-butanol and dowtherm A on the non-catalysed glycerolysis of oleic acid was also investigated, shown in Fig. 8. For all the solvents aforementioned, selectivity towards monoglycerides obtained was above 98%, suggesting solvent usage provides higher MG selectivity. This implies that in particular configuration the addition of solvent led to reduction in autocatalytic reaction (conversion 30%); marking inhibitory effects of the solvents.

Addition of a Tin–Organic Framework Catalyst to the tert-butanol system defined in Fig. 8, increased the oleic acid conversion to 40% maintaining similar MG selectivity [115]. However, lower oleic acid conversions imply that though solvents increase the mass transfer considerably, a catalyst is required to increase the reaction rates. Another plausible reason might be the equimolar ratio of oleic acid to glycerol i.e., not enough glycerol was available for reaction in the oleic acid phase. In addition, the lower glycerol molar feed avoids steric

hindrance of FFA by the glycerol molecules and opens up the FFA molecule for possible reaction with tert-butanol, producing undesired butyl esters. When higher molar ratios of oleic acid to glycerol (1:6) were investigated in the presence of tert-butanol in a tubular continuous reactor, higher MG selectivity (95%) with increased oleic acid conversions was achieved; 30% at 200 °C and 74% at 240 °C, respectively in 2.5 hours [127]. However, in contrast, no significant effects of glycerol to FFA molar ratio, from 1 to 10, with similar reaction configuration were observed when phenol was used as a solvent [128].

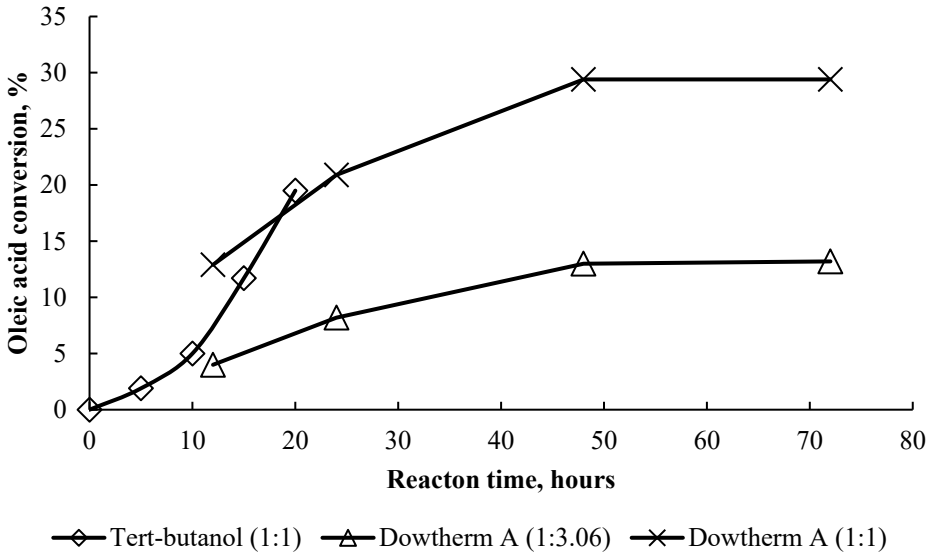


Fig. 8. Performance of solvents in glycerolysis of oleic acid. The ratio in brackets is oleic acid to glycerol molar ratio. For tert-butanol, total reaction mixture: solvent = 1:6.28 (w/w), 150°C and 20 hours of reaction time. For dowtherm A (both molar ratios), 0.1 molar solution of oleic acid in the solvent at 180°C for 72 hours. Data adapted from [115, 116].

Complexities arise in using solvents as well as recovering the solvent. Its recyclability is difficult owing to the reactants' miscibility in the solvent used. Therefore, a solvent with a different boiling point must be selected to ease the separation. Higher boiling point is a prerequisite for any solvent to be used in glycerolysis to limit the solvent vaporization. In terms of green chemistry, the use of the aforementioned solvents adds their intrinsic toxicity in the reaction [122], hence, increasing the environmental footprint of a reaction. Thus, in accordance with green chemistry, either a new class of green solvents should be investigated or the use of solvents from the reaction shall be eliminated. The immiscibility problems in absence of a solvent can be circumvented by optimizing the other reaction parameters such as temperature, pressure, molar ratio and mixing regime, with or without the catalyst.

2.2.5 Agitation unit

Agitation is required to facilitate the interactions between the two reactants that are almost immiscible as discussed in section 2.1.4. Thus, without mixing the reaction is essentially a Liquid-Liquid biphasic reaction. So, to increase the mass transfer, agitation is usually done through conventional means i.e., mechanical stirring in batch reactors. Felizardo et al. studied glycerolysis in a batch reactor and varied the stirring velocity from 300 to 500 rpm [97]. No substantial enhancements in reaction kinetics were observed in this range. This might be due to the axial (vertical) stirring in the lower half of the vessel, unable to enhance homogeneity

within the studied velocity range. Marginal gains in oleic acid conversion were reported when stirring speed is increased from 600 to 800 rpm [110]. The reaction was carried out at 1:6 oleic acid to glycerol molar ratio, 220°C for 5 hours. Thus, many researchers [110, 129], reported 600 rpm as an adequate stirring speed which increases the reaction kinetics. In-depth study of the physical characteristics of the conventional agitation unit has not been found in the literature so far. More energy-intensive mixing regimes like hydrodynamic cavitation and ultra-sonication have been investigated [129, 130]. These methods provide better turbulence which further facilitates reductions in the required molar ratios, temperature, reaction time and enhances performance in comparison with mechanical stirring [132]. These advanced process intensification techniques though to reduce the reaction time by overcoming the mass-transfer limitations imposed on conventional mixing, are at the present moment cost ineffective and require further development [133]. Gogate et al. [134] in their critical review on advanced agitation reactors, concluded that although hydrodynamic cavitation reactors and sonochemical reactors provide advantages as aforementioned but, at the present, the sheer cost and operational requirements make these method unappealing for the industry. Since, glycerolysis is considered as a potential in-situ pre-treatment step, efforts are focused on its maximum efficiency at minimum cost, and thus these advanced methods do not fit the equation.

2.2.6 Glycerol purity

Crude glycerol is basic, with reported pH around 10 while for pure glycerol it is 6.4 [103]. This rise in pH is due to the residual alkaline catalysts from transesterification [135]. This opens up the possibility of alkaline catalysis, which should enhance the base-catalysed glycerolysis, though saponification will decrease the yield and generate additional water molecule. Lyazzat et al. [110], studied the non-catalysed glycerolysis reaction for 300 minutes of reaction time and reported optimum conditions to be 220 ℃, 600 rpm stirring speed, 80 ml/min N_2 purging and 1:6 molar ratio of oleic acid to glycerol for an efficient conversion of approximately 99.7% with a selectivity towards mono, di and tri-olein as 83.1%, 13.0% and 3.5% respectively. However, this was the case only when USP grade glycerol and oleic acid were used. When crude glycerol from soybean methyl esters biodiesel was used, the conversion rates and mono-olein selectivity dropped to 62.9% and 49.7% respectively, indicating that impurities such as water, methanol and sodium salts have adverse effects on glycerolysis [110]. Fig. 9 provides validation of the above point. It is seen that glycerolysis efficiency decreases with the increase in the impurity level of glycerol.

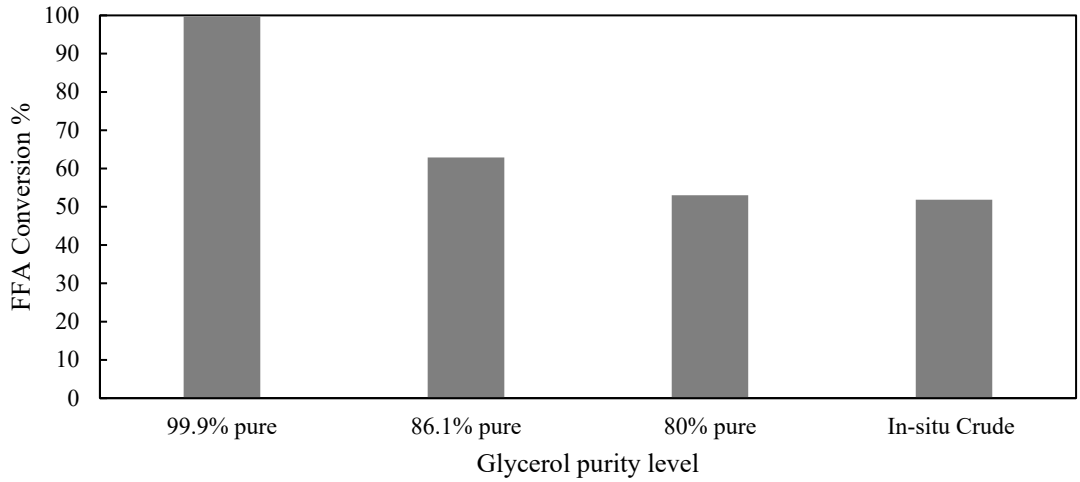


Fig. 9. Effect of Glycerol purity levels on Conversion [110].

The decrease in available glycerol per mole of the crude glycerol, in comparison is one major factor behind the decrease in FFA conversion. Impurities such as methanol, ash, water and soap interfere with the reaction, as discussed here. The characterization of cure glycerol is shown in Fig. 10. Kong et al [136], investigated the effect of impurities in glycerol, on the microwave-assisted glycerolysis of oleic acid. In comparison to the pure glycerol, usage of 70% and 86% purity glycerol was studied. It was observed that the moisture content in the crude glycerol adversely affected the FFA conversion. This was in turn proven when the conversion was higher in the case of 70% purity glycerol than in the 86% purity glycerol; as moisture content for the later grade of glycerol was higher. Also, the water formed during the was swept out of the reaction system by N_2 purging, to keep the reaction in the forward direction. Thus, the presence of additional moisture as an impurity in glycerol, causes a decrease in the yield, as observed in the study aforementioned. This is due to the formation of more FFAs by the hydrolysis of ester linkages; also, it is aided by the hygroscopic nature of glycerol [106]. Low amount of methyl oleate was also detected in the reaction mix, as some methanol in the crude glycerol, reacted with the oleic acid. In addition, if considerable in amount, methanol presence will decrease net available energy content when it evaporates at its lower boiling point.

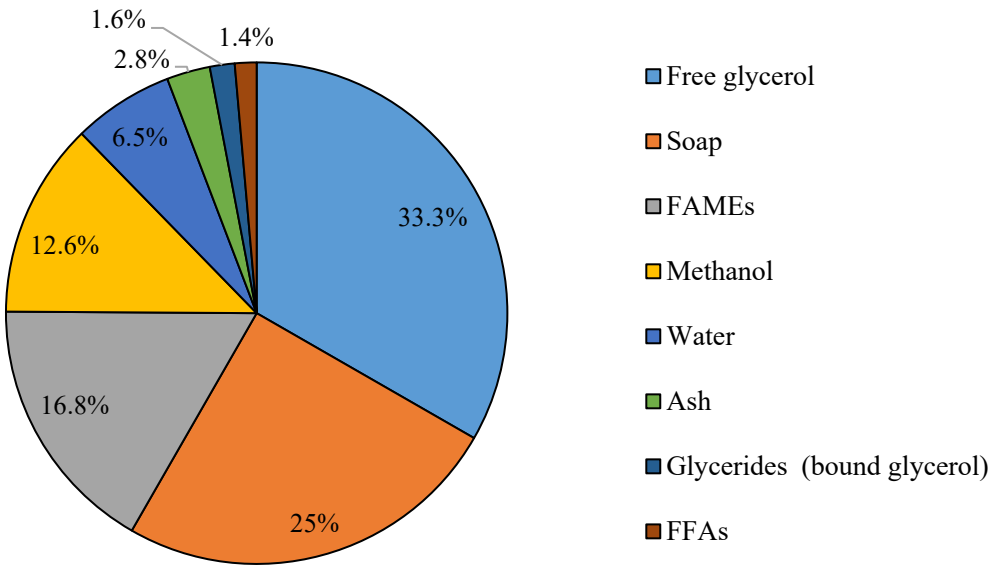


Fig. 10. The approximate composition of crude glycerol obtained from transesterification of soybean oil, adapted from [135].

2.2.7 Catalyst type

In FAMEs production, when FFA content in the feedstock is above 5%, the additional alkaline catalyst is required. This results in a considerable amount of soap formation during transesterification as the FFAs react with alkoxides (i.e. KOH and NaOH) to produce alkaline soap, as discussed in section 1. To effectively treat lower quality feedstocks, acid-catalysed esterification of FFAs to alkyl esters avoids saponification and thus, this process has been recognised as a pre-treatment step in the present biodiesel production scheme [102]. Pouilloux et al. [126], emphasised this very choice between alkaline and acidic nature of catalysis in their study where they esterified stearic acid in the presence of sodium carbonate and para toluene sulfonic acid (PTSA) as well as without any catalyst, as shown in Fig. 11. Without a catalyst, FFA reduction is less than 30%; however, the conversion increases when a catalyst was used. Amongst the catalysts used, PTSA exhibits almost double the conversion as compared to that of sodium carbonate. A possible reason behind the lower conversion in case of the sodium carbonate is the saponification side reactions, resulting in the loss of the desired product, as discussed above. However, in the glycerolysis product, MAG content is higher for sodium carbonate (68.5%) than for PTSA (32.3%), showing the higher selectivity of the basic catalyst for monoglycerides at 110°C. Reason for such observation is that the relative reactivity of the 1° and 2° hydroxyl groups of the glycerol towards mono-esterification and di-esterification, is depended on the basicity of the catalyst [126], which is expected to be more for sodium carbonate.

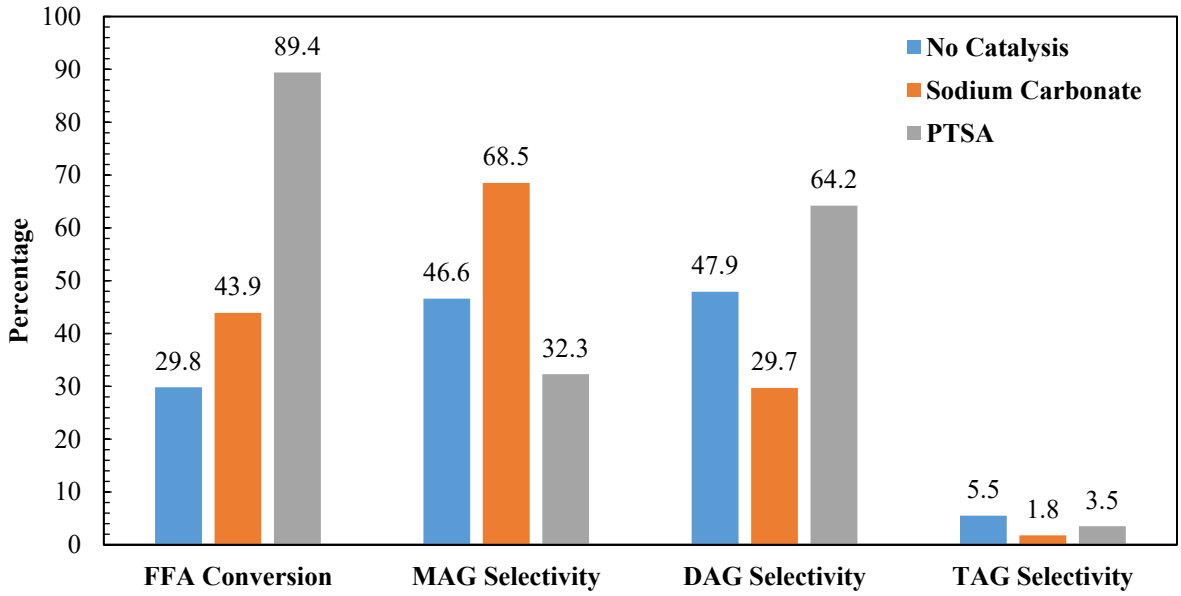


Fig. 11. Performance for most conventional glycerolysis reaction routes [126].
T= 110°C; catalyst wt. = 0.5 g; glycerol/ stearic acid = 1; Time = 16 hours.

2.3 Problems associated with glycerolysis

So far, it has been established that, for the glycerolysis reaction to proceed effectively, high temperatures, longer reaction times, vigorous stirring and continuous water removal are required. The reaction is reversible and requires rapid ice-cooling to bring down the temperature of the reactor to eliminate any chances of the reverse reaction, near completion to maintain the desired products [137]. In comparison to methanolysis or ethanolysis, glycerolysis is a more complex reaction due to the polyhydric function of glycerol [116].

The problems associated with the use of glycerolysis reaction are summarized as follows:

1. Glycerol is a bulky polyalcohol, thermally stable and a weak nucleophile in a nucleophilic acyl substitution reaction [11, 129].
2. Glycerolysis is reversible [138], thus requires the use of catalyst.
3. The need of catalyst removal/neutralisation that is energy-intensive in a homogenous catalyst system is common while using a heterogeneous catalyst, there is a multi-phasic system having an improper degree of contact between catalyst and reactant [63].
4. The reaction takes place in the organic phase and there is a negligible amount of reaction in the glycerol-rich phase [139].

The acyl part of fatty acids: *R*-C=O, needs to be attacked by glycerol. The primary strategy to alleviate this is to use a catalyst for protonation of the fatty acids` carbonyl group, followed by an electrophile-induced nucleophilic attack of the α-hydroxyl bonds in glycerol to make it a better nucleophile [140]. Consequently, producing glycerides and creating water as a by-product. The next step in this review is to consider the different types of catalytic systems reported in the literature, for the glycerolysis of FFAs.

3 Catalysis

The need for the catalysis in the glycerolysis arises from the fact that catalysis application will offer an energetically favourable pathway. This implies a reduction in the reactor size with milder reaction conditions in terms of temperature and pressure could be possible. At the same

time, a catalyst increases the selectivity towards the desired products and reduces the production of by-products.

Broadly, there are three types of catalyst classes: enzyme/bio-catalysis, heterogeneous and homogenous catalysis; while the combination of these types generally categorised under hybrid catalyst class. In general, industrial applications, glycerol esterification is primarily done by employing homogenous catalysis such as mineral acids for producing MAG [140, 141]. However, the homogeneous catalysis requires intensive downstream purification and separation units, thus generating large quantities of waste downstream [102]. Enzymatic catalysis offers milder operating conditions with wider substrate flexibility and higher product selectivity (MAG), followed by simple purification processes [143]. However, the higher cost of enzymes, lipase inhibition due to impurities, longer reaction times and need for other components such as solvents or reaction media make enzymatic catalysis infeasible at this present stage [91]. Heterogeneous catalysts have more stability and can be made from low-cost ingredients such as waste biomass [144-146]. Moreover, in a continuous production system, both homo- and heterogeneous catalyst can perform simultaneous esterification/transesterification reactions [59]. Nevertheless, the costly preparation, leaching in the reaction medium and post-reaction recyclability remain a challenge for the heterogeneous catalysis. Deteriorations of the catalyst such as catalyst leaching and inhibition due to the reactants or by-products decrease their efficiency. Being a three-phase system there are limits to mass transfer increasing in the reaction times and temperatures [147].

3.1 Enzymatic catalysis

Of the three types of catalysis, enzymatic catalysis is the least commercially used catalysts in the biodiesel production due to its high cost [148]. Although glycerolysis can be done chemically with acid or base catalysis, enzyme catalysis provides the best-in-class benefits: mild operating conditions, minimal side-reactions and increased selectivity for desired products [149]. Lipase catalyses fatty acids in the presence of alcohol to produce esters and water [150]. Lipozyme IM-20 was reported to successfully esterify acid oils to the respective fatty acid esters of short and long-chain alcohols in a dual-step enzyme catalysed reaction at high yields [151]. Kahveci, 2009 [152] tested ionic liquids as a substitute media for enzymatic glycerolysis of Triolein for DG synthesis using Novozym 435, Lipozyme RM IM and Lipozyme TL IM as lipases. 45% diglycerides yield in 12 hours were observed for ionic liquid, trioctylmethylammonium bis (trifluoromethylsulfonyl)imide [TOMA·Tf_2N], while 43% diglycerides yield in 12 hours were observed when Ammoeng 120, a quaternary ammonium sulfate, were used respectively. In all the 17 types of ILs studied, only 1-methyl-3-octylimidazolium hexafluorophosphate ([OMIM][PF6]) and [TOMA·Tf_2N], was able to provide proper mixing of reactants and provide a suitable microenvironment for the lipases to work. The suitability of these ILs originates from their cations and anions. The ILs were able to bind the hydrophobic glyceride molecule with a hydrophilic glycerol molecule. The bulkiness of cation molecule may be attributed for this. Prior to the glycerolysis, emulsification of the substrates also improves the efficiency in a lipase/oil/glycerol phase. This has also been demonstrated in case of sardine oil catalysis using Lipozyme 435 [153]. When the experiment was carried out using the super-critical carbon dioxide (SC-CO_2) as the reaction medium, the same study also found that the change in pressure (15 to 25 MPa) has no positive effect on the reaction. However, increasing the temperatures from 40 to 90°C increased reaction rates in both systems. Though, the reaction pressure should have a significant effect to the diffusivity

of oil in the reaction medium, no pressure effect was observed. This might be due to the diffusion of the triglycerides into the SC-CO_2 medium, rendered it not available for the reaction.

Bio-silicification, a process to encapsulate lipases in SiO_2, was anticipated to improve the activity and reaction efficiency in comparison to the unsupported enzymes by providing the improved mechanical and thermal stability, which would improve the catalyst recyclability [154]. Pervaporation process can be used to remove water to enhance the reaction [155]. Some of the studies on enzymatic glycerolysis are summarised in Table 2. In Table 2, it is found that the ultrasonic pre-treatment is a good option for reducing the reaction times, in addition to the emulsification of the reactants. It provides many enhancements for the reaction rates. Of all the lipases studied, Novozyme 435 gave better conversion which increases when lipase is supported [156]. ChCl- based DESs successfully solvates the enzyme catalysis, providing the highest conversion (91.80%) and yield (85.22%) in comparison to other organic solvents such as dimethylsulfoxide and other ionic liquid used [157].

Table 2
Summary of the notable literature for the Lipase catalysed glycerolysis.

Lipase	Optimum Conditions	Conversion %	Selectivity %			Remarks	Ref
			MAG	DAG	TAG		
MAS1 (strain W007 from marine Streptomyces sp.)	Lipase loading of 163.8 unit/gm substrate, 4.13:1- Ethyl Ester: glycerol molar ratio at 65°C, achieving a final acid value of 0.03 mg KOH/g in 24 hrs.	82	15.6	7.9	76.5	Non-regioselective MAS1, immobilised on to a particular resin is used in facilitating glycerolysis of ethyl esters in producing n-3polyunsaturated rich triglycerides. The study is mostly aligned with the food processing industry, however, shows that enzymatic catalysis possesses great scope in the glycerolysis area, thus in biodiesel production. However, at the same time, the time of reaction is somewhat unsuitable for industrial biodiesel applications.	[158]
Lipozyme® RMIM	Pre-treatment - ultra-sonication at 45°C for 5 minutes at 250-Watt power. Lipase-Lard ratio 4:100 on a weight-to-weight basis, then 4 hrs of glycerolysis reaction at 50°C with 180 rpm.	76.88	-	46.91	-	Pre-treatment step reduced the reaction time from 11 hours to 4 hours after an initial 5 minutes of ultra-sonication. However, probe cost and energy input in a pre-treatment step must be accounted as well for better understanding, since no other difference is seen in products or reaction.	[155]
Novozym 435 (acrylic resin immobilised CalB)	3-5 wt. % lipase at 60°C for 12 hrs in 50ml round-bottom flask containing 30gm high-acid soybean oil with 2.4gm glycerol agitated at 500rpm with N_2 purging. The acid value of oil =50.	98.8	12.37	69	18.38	Effect of glycerol concentration was null on DAG, but TAG and MAG content improved in products. Stability of lipase was good for ten cycles of reuse, without loss in its activity.	[156]
Organic-modified SBA-15 Immobilised Lipase Rhizomucor miehei (RML)	0.2gm modified lipase in 0.184gm glycerol to 3.52gm soybean oil at oil bath (60°C) with 200rpm magnetic stirring for 24 hrs.	84.24	29.36	54.88	-	The study reveals that organic modification in immobilising the lipase on mesoporous silica, significantly improves overall reaction activity, selectivity and stability. Effect of the organic group attached to SBA-15 RML, is studied. It is seen that with increasing carbon groups in the organic part, DAG/MAG ratio decreases. Benzyl-SBA-15 RML showed the least DAG/MAG ratio=1.99.	[160]
Candida antarctica lipase B (CALB) is modified with –	Glycerol/ palmitic acid – 4:1, 20 mg Molecular sieve and 4 ml acetone, incubated at 50°C at 300 rpm. 50µl of modified lipase.		48	1.4	0	High activity preparation of lipase increased the performance. High MAG selectivity is obtained than previous studies. Conversions were not reported.	[161]
1. Cross-linked enzyme aggregates (CLEAs)	For un-modified lipase reaction time- 24 hrs. For modified lipase reaction time-12 hrs.	-	81	4.5	0	Use of polar solvent, acetone and comparatively shorter residence time of 12 hrs, was a probable reason behind lower DAG content.	
2. Protein coated microcrystals (PCMCs)			82	4	0	Thus, polar solvents aid to the MAG formations. Use of molecular sieves increased the conversions for both MAG and DAGs.	
3. Cross-linked protein coated microcrystals (CLPCMCs)			87	3.3	-		
Immobilised lipase PS-DI from Burkholderia cepacia	Glycerol/anchovy oil molar ratio – 3:1, with 9.0 % (w/w) lipase without a solvent. 45.8°C, 200rpm for 4hr.	76.90	24.32	52.99	-	The study operated in the solvent-free system keeping a focus on oxidative stability of the products for the first time. They achieved a significant 68% increase in induction time from 0.84hour. Oxidative	[162]

						stability is vital in the industrial application of glycerolysis, and thus this study is crucial. Factors affecting the oxidative stability are Gly/TAG molar ratio, reaction conditions, TAG composition, among others.	
Novozym 435	T= 65°C, methyl caffeate (MC) =50g/l, MC/lipase=1:5 (w/w), DES/Gly=1:10 (v/v), 180rpm, flow rate- 2µl/min, residence time of 2.5hr in continuous flow micro-reactor.	96.46	-	-	-	Enzymatic glycerolysis of caffeic acid in a 5ml micro-reactor with a co-solvent DES (Choline chloride: urea). On comparison with the batch reactor in a conventional system, time is reduced by 75% and yield up by 6%.	[113]
Novozym 435	Enzyme load 8%, 8 hr reaction time, DES dosage 10%, TAG/glycerol molar ratio 1:4, 80°C and zero saturation.	75.80	-	65	-	DAG production from soybean oil is studied in presence of glycerol-based DES. Out of ChCl, ethanol and butanol, ChCl and glycerol at 1:2 molar ratio, showed the best capability as reaction medium with no water added. Lipase reusability obtained is up to 5 times.	[157]

- data are not available.

3.2 Heterogeneous catalysis

Due to easy separation and recovery of the catalyst, this class of catalysts is widely adopted industrially. The main challenges for homogeneous catalysts are durability, reusability, cost-effectiveness and greenness of the process. Various heterogeneous catalysts suffer from extensive and costly catalyst preparation or deactivation due to their stability problems, inhibition by impurity or the reactant, or the poor structural design [163].

Considering the case of the metal oxides, metal (M) oxides (O): M-O solid acts as a weak Lewis acid (M) and strong Brønsted base (O) pair. Building up on M-O catalysed methanolysis mechanism proposed by Cristina et al [164], a mechanism for glycerolysis is proposed as following: Initially, the hydroxyl group at α-carbon positions, the hydroxyl group at 1 and 3 positions being more available than β-position carbon owing to steric hindrance with glycerol molecule, is activated by the catalyst. Consequently, H^+ is bonded by O_s site and the remaining glycerol anion ($C_3H_8O_3^-$) is bonded to M_s site on the catalyst surface. Simultaneously, owing to resonance in the acyl group of fatty acid, there is a partial positive and negative charge on the C=O double bond. This is also bonded weakly on M_s site [165, 166]. The role of M_s site is to stabilise the negatively charged reaction intermediates, glycerol and fatty acid, while O_s site is there to extract the proton from alpha hydroxyl group in glycerol. After this, desorption of intermediates take place in which water and the desired product gets generated, and the catalyst is again available for the next cycle. In heterogeneous catalysis, many other mechanisms are possible and have been studied [164-168].

$ZnCl_2$ catalysed glycerolysis of the waste FFAs was studied by Mostafa et al [137]. Using a batch reactor at 195°C, 500 rpm of stirring speed and equimolar reactant mixture fed with 0.3 wt. % of $ZnCl_2$ gave over 99% FFA conversion in just 100-minute mark. The same authors also studied the extent of the reversible reaction and the effect of three different cooling mechanisms in stopping it. The final FFA content after employing different cooling mechanisms including air-cooling, water-cooling and refrigeration cooling was 87%, 97% and 99%, respectively. This shows that rapid cooling is necessary, to quickly separate the glycerol phase from the FFAs and stop the reaction effectively. The difference between the rate of sample cooling and thus the cooling time taken, is proportional to extent of reversible reaction that can happen. Therefore, the extent of reversible reaction is higher when air-cooling is used and lowest when rapid cooling is used. The same authors also did process simulation using ASPEN HYSYS, to analyse the scale-up effects of using the fatty acids up to 100 tons daily. This resulted in 96% ester and 4% glycerol as the products, at the bottom of the distillation unit. 73% of unreacted glycerol was recovered at top of the distillation tower. When Zn and Zn-acetate were used as the catalysts (0.1 wt. %) in the glycerolysis of an acidulated soap-stock, similar temperature (200°C) and molar ratios resulted in 93% FFA conversion in 60 minutes [97]. The results in these reported studies somewhat differ, however it can be said that using metallic catalysts enhances the reaction kinetics, in the otherwise longer reaction.

In Table 3 metal oxides (ZnO, MgO, SnO), metal halides ($BuSnCl_3$, $ZnCl_2$), modified metal organic frameworks (M. Mofijur, #33) and other heterogeneous catalysts used for glycerolysis found in the literature have been listed. In the case of $SO_4^{2-}/ZrO_2–Al_2O_3$, a sulphated metal oxide complex, though the conversion was over 98%, almost equal distribution of product into MAGs, DAGs and TAGs was obtained [172]. A possible reason behind this low MAGs selectivity might be longer reaction time (4 hours) and inefficient which may cause increased MAG to DAG or TAG conversions. Further investigations on the effect of higher molar ratios

of reactants, might have been done, to reflect on the product distribution. Perhaps, this might be due to the lesser selectivity of the complex.

Complete conversion of the oleic acid to glycerides was obtained, when the tin–organic framework (Sn-EOF) was used as a catalyst with reaction conditions, 1:10 oleic acid to glycerol molar ratio and 1 wt.% catalyst at 180℃ [115]. However, even non-catalysed glycerolysis gave 89% conversions as well. Hence, the effect of Sn-EOF, was superimposing only. Similarly, for other MOFs used in the same study, similar catalytic activity as that of a non-catalysed high temperature glycerolysis reaction was obtained. It was clear from the study that the glycerolysis reaction conditions are less suitable for catalysts with $Cu_3(BTC)_2$, a metal-organic framework consisting of copper metal ions and benzyl trimesic acid as the organic linker; this was due to its degradation and subsequent mixing in the reaction. This might be due to the fact that $Cu_3(BTC)_2$ and it modified forms are more suited to catalyse ester hydrolysis reaction pathway [173]. Hence, these applied operating conditions might not have been in the catalysts` operating range or further optimization of the catalysed reaction could be done on the current parametric range. Oleic acid at the temperature above 150°C, causes degradation of Sn-EOFs and thus temperature was limited to 150℃ to preserve the catalyst and thus conversion reduced to 26% and 40% in 8-hour and 20-hour reaction time, respectively. The application of MOFs in the presence of tert-butanol solvent shows good catalytic activity. Problems due to the reactants, such as degradation by oleic acid and inhibition by glycerol are also some of the issues with heterogeneous catalysts. Acidic ionic-exchange resins show higher selectivity towards monoglycerides [101, 170] but with the restriction in temperature as they are prone to swelling in the reaction mixture [175], limits their applications.

Table 3
Studies reported in the literature for the heterogeneous catalyst performance and reaction conditions in glycerol-esterification with FFAs.

Catalyst	Feedstock	T[a] (°C)	G: F[b]	Time (min.)	Conversion %	MAG %	DAG %	TAG %	Remarks	Ref.
Sulfated Zirconia Loaded SBA-15 Catalyst (0.58 g of $ZrOCl_2.8H_2O$ with 16 wt% loading)	Lauric acid	160	4:1	360	94.9	83.4	5.61	1.79	Investigators incorporated sulfated $ZrOCl_2$ onto SBA-15 to get improved mesopore surface area. Due to lower micropore area and increased $ZrOCl_2$ content in the heterogeneous catalyst, the molecular-sieving effect was observed. This sieving effect enhanced the esterification reaction.	[176]
Sulphated SBA-15	Lauric acid	160	4:1	420	94	70.2	23	2	At 5 wt.% catalyst loading, successful glycerolysis of lauric acid has been done, under reduced pressure (0.65 bar) in a batch reactor. Reusability up to four cycles was obtained.	[177]
12 tungstophosphoric acid ($H_3PW_{12}O_{40}$) SBA-15	Lauric acid	160	4:1	360	70	50	-	-	Successful addition of HPW anions into SBA-15 was reported to increase catalytic performance. Higher than 20wt% of HPW resulted in choking of pores, resulting in a decrease in performance.	[178]
Solid superacid $SO_4^{2-}/ZrO_2–Al_2O_3$	WCO (initial Acid value ~88 mg KOH/g)	200	1.4:1	240	98.4	31.1	28.7	39.6	Apart from inherent metal toxicity in the catalyst, this process achieves good conversion with easy separation of catalyst and glycerol from the product, with a low catalyst loading of 0.3 wt.%. However, such high temperature and complex catalyst preparation increase reaction expenses.	[172]
ZnO Catalyst loading (0.5% w/w)	Oleic acid	150	4:1	360	62.82.68	70.21	25.12	4.67	Heterogeneous ZnO-Zeolite was studied in this paper. Besides, a kinetic model is proposed to explain the main and side reactions. The study reported place of the reaction is in oleic acid-rich phase, while glycerol extracts the produced water during the reaction to help shift the reaction in the desired direction. Leaching is reduced due to zeolite supporting.	[139]
ZnO + Zeolite support Catalyst loading (0.5% w/w)		150	4:1	360	89.85	67.41	28.40	4.19		
MgO	Stearic acid	160	1:1	1440	67.5	60.8	37.5	1.7	Comparative studies on the effects of applying basic and acidic catalysts were done in this study. Basic catalysts can limit secondary reactions and decrease product conversion percentage. ZnO was found to be a better solid basic catalyst as others are more prone to	[126]
ZnO		160	1:1	1440	36.5	79	20	1		
ZnO with solvent diglyme		110	1:1	960	63	82.5	17.5	-		
ZnO with solvent diglyme	Lauric acid	110	1:1	960	56.1	73.3	26.7	-		

Catalyst	Feedstock	T[a] (°C)	G: F[b]	Time (min.)	Conversion %	MAG %	DAG %	TAG %	Remarks	Ref.
ZnO with solvent diglyme	Oleic acid	110	1:1	960	45.1	90.7	9.3	-	saponification. Diglyme presence in ZnO catalysis further enhances its activity and selectivity, showcasing that reagent`s and product`s, solubility and solvation, are important in glycerolysis. In addition, in diglyme, the activity of ZnO is affected by the composition of fatty acids, being highest in stearic and lowest in oleic acid.	
[Me/SO_3H]–MCM-41 mesoporous material	Oleic acid	150	1:1	360	96	41.6	-	-	Modified MCM-41, is charged with simultaneously with sulfonic acid and alkyl groups to make a hybrid catalyst. It is reported that tuning the alkyl/sulfonic acid ratio in catalyst affects the activity, 1.8 milli-equivalent Me (methylation)/ gm of catalyst is optimum for 63% of monolaurin content. The effect is less pronounced in oleic acid glycerolysis.	[179]
[Me/SO_3H]–MCM-41 mesoporous material	Lauric acid	120	1:1	480	92	68	-	-		
Coated silica gel-SO_3H	Lauric acid	112	1:1	720	97	51	-	-	Monolaurin synthesis via siliceous mesoporous modified materials like silica gel, HMS (hexagonal mesoporous silica), MCM-41 and H-USY (ultrastable Y) zeolite is done. These materials are modified with propyl-sulfonic acid groups. Study of catalyst synthesis via different routes and their effects on catalytic activity and efficiency was reported. In the esterification process, reactants are fed into 100 ml round bottom flask heated at 200 rpm and catalyst loading of 5wt. % with respect to glycerol is done. Silica gel coated with propyl sulfonic acids had better FFA conversion profile but as with others, MAG selectivity is not much. This is due to the autocatalyzing effect of lauric acid, it reacts with MAGs to produce DAGs and TAGs.	[180]
HMS-SO_3H				1320	91	52	-	-		
Silylated MCM-41-SO_3H				1440	81	53	-	-		
Coated MCM-41-SO_3H				1440	77	47	-	-		
Amberlyst-15				708	72	44	-	-		
Zeolite H-USY (Si/Al=14.5)				1410	55	36	-	-		
Layered double hydroxide - complex $MgAlCO_3$	Oleic acid	160	3:1	180	90	65	33.7	1.-3	2 wt. % of catalyst gives the best conversion without having product browning as seen at 180°C, concerning the food industry.	[168]
Blank	Oleic acid	120	1:1	180	30	75	24	1	When tert-butanol was used as a solvent for homogenising the tin-organic framework (Sn-EOF), leaching was limited and catalyst stayed active. However oleic acid was responsible for catalyst degradation at high temperatures, above 150°C. The metal centre acts as a Lewis acidity catalytic centre and is behind the catalytic activity. Over 98% MAG selectivity with 40% conversion is achieved at 150°C,	[115]
		180		180	89	51	40	9		
				480	45	62	35	1		
HPW/$Cu_3(BTC)_2$[d] (1wt% loading)		180		180	97	39	49	12		
Nano HPW/ $Cu_3(BTC)_2$		180		180	99	21	35	9		
HSiW/$Cu_3(BTC)_2$		180		180	88	50	43	7		

Catalyst	Feedstock	T[a] (°C)	G: F[b]	Time (min.)	Conversion %	MAG %	DAG %	TAG %	Remarks	Ref.
Ultrastable Y zeolite (1wt% loading)		120		480	45	63	34	3	but in the absence of solvent 100% conversion and 48%, MAG content is reported. Thus, it is seen that in presence of solvent the monoglycerides to di- and triglycerides conversion is halted due to separation of product as they are formed, from the catalytic centres.	
		180		180	92	47	43	10		
Sn-EOF (in metal- organic framework, where 4,40-dibromobiphenyl is organic linker)		180		180	100	48	42	10		
Sn-EOF with solvent- tert-butanol		150		480	40	98	2	0		
$BuSnCl_3$	Oleic acid	180	1:1	180	87	49.4	40.2	10.34	Various organotin (IV) compounds were studied for glycerolysis of oleic acid. At 0.01 moles of catalyst w.r.t glycerol, activity is in order- $BuSnCl_3$ >Bu_2SnLau_2 >Bu_2SnCl_2 >Bu_2SnO >BuSnO(OH). It was concluded that the most active catalysts act as typical Lewis acids ($BuSnCl_3$, Bu_2SnLau_2, and Bu_2SnCl_2) while the least active ones follow ligand exchange concept (Bu_2SnO and BuSnO(OH)). A higher stirring rate was used (2000rpms).	[181]
Bu_2SnLau_2					79	58.22	37.9	3.8		
Bu_2SnCl_2					78	56.4	35.9	6.4		
Bu_2SnO					71	54.5	38	8.4		
BuSnO(OH)					65	36.9	47.7	15.5		
Catalyst dosage (.01mole with 1:1 reactant mixture)										
Ion-exchange resin[e] - Amberlyst 31	Oleic acid	90	6:1	1440					The reaction is carried out in glass batch reactor agitated at 800rpm with 7 wt.% catalyst. Four resins and effect of swelling on their conversion and selectivity is studied. Swelling in reactants or water or a solvent is considered. For Amberlyst 31 swelling in glycerol increased its selectivity but significantly reduced its conversion ability, this might be due to selective inhibition. While swelling in oleic acid had positive overall effects. Water had a significantly detrimental effect on results, with 88% drop in conversion for Amberlyst 31. It is removed by molecular sieving (3 Angstrom) after which conversion increased by 1.32 times. Increasing carbon chain length decreases conversion rate due to lesser accessibility to active sites in resin.	[101, 170]
without swelling					68	80	17	3		
with swelling					75	82	14	4		
Amberlyst 16										
without swelling					37	83	12	5		
with swelling					42	77	19	4		
K1481										
without swelling					49	78	21	0		
with swelling					45	83	17	0		
Fe–Zn double-metal cyanide (7 wt.%)	Lauric acid	180	1:1	60	75.0	66.0	28.8	5.2	During the catalyst synthesis, the temperature at which the $ZnCl_2$ solution was added to the potassium ferricyanide solution had marked positive effect on the surface area, which affected the product yield. Water addition up to 0.5 wt.% resulted only a slight decrease in yield due to hydrophobicity of catalyst. Catalyst retained the yield for 2 consecutive cycles.	[182]
	Myristic acid				75.9	69.4	24.0	6.6		
	Stearic acid				62.2	77.7	19.0	3.3		
	Oleic acid				63.4	67.3	31.7	1		
Hydrophobic ZrO_2-SiO_2-Me&Et-$PhSO_3H$	Oleic acid	160	1:1	240	80	59.4	34.6	6.0	Increasing temperature and catalyst concentration decreased MAG selectivity. Catalyst acid strength and availability of these acid sites on surface influence yield whereas the pore volume and induced hydrophobicity to	[183]

Catalyst	Feedstock	T[a] (°C)	G: F[b]	Time (min.)	Conversion %	MAG %	DAG %	TAG %	Remarks	Ref.
									zirconium catalyst dominates the selectivity in the end product. When the reaction time was doubled, ~8% increase in conversion was seen with lowered MAG selectivity, due to MG further converting to DG and TG.	

- data are not available.

[a] Reaction temperature.

[b] Glycerol to FFA (feedstock) molar ratio.

[c] Technical Olein is from the vegetable oil refining process.

[d] HPW/ $Cu_3(BTC)_2$ catalyst- copper benzene tricarboxylate MOF having encapsulated HPW.

[e] swelling in oleic acid for all resins.

3.3 Homogenous catalysis

Homogeneous catalysts perform better at catalysing the reaction as they provide faster reaction rates as all the reactants, including the catalyst itself, are in the liquid phase [184]. The corrosion of equipment, side-reactions and difficulty in separation are few associated problems with homogenous catalysts [185].

Researchers have used sulphuric acid, PTSA, heteropolyacids and other similar catalysts for homogeneous acid-catalysed glycerolysis. These homogenous catalysts behave as a protonating agent in the reaction [186]. For alkaline catalyst, NaOH (1.75 wt. %) was studied in the re-esterification of crude jatropha oil [187] and crude castor oil [188] with glycerol. The conversions of over 99% were obtained only around 60°C with an equimolar feed for 75-85 minutes. Dani et al [189], investigated effects of a co-solvent (hexane) in NaOH catalysed-glycerolysis of WCO with acid value 12mg KOH/g. 1.3% of NaOH in hexane with oil to co-solvent weight as 2:1, reduced up to 92% acid value in 20 minutes. However, the strict regulations on using petro-derived solvents such as hexane cause applicability problems [190].

Modifying heterogeneous catalysts with homogeneous catalysts leads to the development of a physically heterogeneous and chemically homogenous hybrid catalyst [191]. Isahak [192] synthesised silico-tungstic acid in bulk (STAB) and silica sol-gel (STA-SG) for esterification of glycerol with oleic acid at 100°C for 8 hours at oleic acid to glycerol molar ratio of 6:1 and then compared the results with homogenous sulphuric acid. H_2SO_4 and STAB produced total conversion of 100% and 98%, respectively, but were lower in MAG selectivity; approximately 81% and 90% respectively. Nevertheless, silica sol-gel modified silico-tungstic acid showed a higher conversion of 94% and a higher selectivity of 95% for monoolein. Higher selectivity of STA-SG is due to the increased number of active sites, due to a higher BET surface area of STA-SG (460 m^2/g) in comparison to STAB (0.98 m^2/g). Also, STA-SG was easy to separate after the reaction, as it was insoluble in the product. Studies conducted in this area are listed with remarks in Table 4.

Observations regarding the effect of free fatty acid chain length on product yield were reported by Kotwal et al, [182]. FFA conversion was directly in proportion with the solubility of the respective FFA in glycerol, as is shown in Fig. 7. This confirms that reactant miscibility i.e., the mass transfer, has a significant effect on product yield and the reaction kinetics.

In the case of the basic Ionic liquids 1-Butyl-3-methylimidazolium imidazolide ([Bmim]Im) [193] as reported in Table 4, it has comparable basicity to KOH and [Bmim]OH, when pH values of their aqueous solutions were evaluated. However, the yield in case of the latter two was lower, with 30% and 3.6%, respectively. As per the authors, the difference between KOH and IL can be understood based on the dispersibility of the two. [Bmim]Im, due to its structure is better dispersed throughout the reaction mixture in comparison to KOH. While, in the case of 1-Butyl-3-methylhydroxide ([Bmim]OH), early degradation was observed at 90°C, thus limiting its capability in reaction.

Recently, deep eutectic solvents (DES) has been increasingly researched in the chemical synthesis field, owing to their potential as green solvents with inherent advantages such as low vapour pressure, biodegradability and being their tune-ability [194]. DES consists of a mixture of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), which when heated together in a specific molar ratio, yield a eutectic mixture. The DES based on quaternary phosphonium salt and PTSA showed lower selectivity towards MAG and more selectivity

towards DAG [129]; this is listed in Table 4. This preference towards diglycerides could be understood from the perspective of Brønsted-acidity like the behaviour of the acidity in DES, which favours diglycerides more than mono-glycerides. A similar observation was made in case of PTSA in subsection 2.2.7.

Extending this study, Zhang et al. [195], studied the same DES in glycerolysis of vegetable oil deodorised distillate, a reject from the edible oil refining industry. They obtained 90% FFA conversion, considering optimum conditions being 160 ºC, 5wt% DES loading, and 10 min reaction time. The presence of water reported in their work limits the equilibrium conversion at 90%. Further investigation in this reaction specifically in effective water removal might be looked into to increase equilibrium conversion.

To summarize on the catalyst performance, the FFA conversion profiles were plotted in Fig. 11 for different sets of homogeneous and heterogeneous catalysts. Organo-functionalised catalysts such as coated silica gel-SO_3H and HMS-SO_3H esterified lauric acid at 112°C, achieved 90% conversion in approximately 10 hours. For the similar conversion, homogenous catalysts [Bmim]Im and Phosphonium based DES take lesser time, 4 hours and 0.5 hours, respectively. However, the selectivity towards monoglycerides is an important aspect as well. Homogenous catalysts show inferior MG selectivity as compared to heterogeneous catalysts. Future research studies may be invested in exploring better selectivity in homogeneous catalysis or perhaps the development of a hybrid catalytic system adopting advantages of both homogeneous and heterogeneous catalysts.

Table 4

Studies reported in the literature for the homogeneous catalyst performance and reaction conditions in glycerol-esterification with FFAs.

Catalyst	Catalyst loading	Feedstock	T[a] (°C)	G: F[b]	Time (min.)	Conversion %	MAG %	DAG %	TAG %	Remarks	Ref
HPW	2.5 wt.%	Lauric acid	160	4:1	240	97	59.8	-	-	Despite higher conversion monoglycerides selectivity is less. Initially, the yield was around 65% at the 120-minute mark but gradually dropped to 61% at the end. This drop is due to lauric acid reacting with monoglycerides to form di- and triglycerides.	[178]
H_2SO_4	8ml/L	Lauric acid	90	6:1	330	69	-	-	-	In comparison to $ZnCl_2$ (66.8%) used in the study, a slight increase in conversion is obtained. This might be due to the mass transfer limitations of the heterogeneous catalyst.	[196]
H_2SO_4	0.01mole with 1:1 reactant mixture	Oleic acid	180	1:1	180	60	56.7	38	5	Higher stirring rate is used (2000 rpm). With the same catalyst and similar loading strategy as above, change in molar ratio and carbon chain length in reactant affects the thermal energy required.	[181]
p-toluensulfonic acid	0.5% w/w	Oleic acid	100 120	1:1	360	100 60	<30 36	- -	- -	Lesser selectivity towards MAGs, in the case of acidic catalysts is observed.	[197]
NaOH KOH	0.5% w/w) glycerol:NaOH soap = 1:1:0.07 (mol) 0.5% w/w) glycerol:KOH soap = 1:1:0.07 (mol)	[a]$C_{12:0}$ $C_{14:0}$ $C_{16:0}$ $C_{18:0}$ $C_{12:0}$ $C_{14:0}$ $C_{16:0}$ $C_{18:0}$	150	1:1	318 360 384 444 432 462 486 546	- - - - - - - -	48.3 48.2 48.4 49.4 47.4 46.3 46.8 46.3	- - - - - - - -	- - - - - - - -	Effectiveness of alkaline soaps in the esterification of fatty acids from medium to long-chain has been investigated. The soap formed during transesterification is intended to be diverted to glycerolysis for catalysing the esterification reaction. With varying catalyst dosage and temperature, no appreciable difference in conversion and yield of different fatty acids, when analysing irrespective of reaction time. However, a descending trend in rate constants is observed with increasing chain length in fatty acids. This could be the reason behind higher reaction time required in the case of longer chain fatty acids, for achieving similar yields. Fatty soaps formed in the first step, increase the rate of reaction and also provide emulsification of glycerol in them. The reaction was done under vacuum (0.8 Bar) to eliminate the water generated.	[198]
NaOH	0.5% w/w	Waste Cooking Oil (initial acid value of 124.9 mg KOH/g)	210	1.4:1	240	99.6	56.5	25.2	17.5	For the first run, NaOH is added to a vacuum pressurised (.05 bar) esterification unit and there onwards it uses alkaline soap. Remarkably, the soap-maintained activity for 13 times and no separation of catalyst and glycerol excess needed for transesterification. The energy required for additional	[199]

										processing of WCO, in terms of heating (200°C), in this study or in general is higher than the regular processing cost in the transesterification method. Nonetheless, up to 45% savings are obtained, since there has been saving in feedstock and catalyst cost by using WCO, crude glycerol and alkaline soap back in the process. More development in the application of alkaline soap recycling is needed.	
([Bmim]Im)	8 wt. %	Soybean oil (0.51 mg KOH/g)	170	6:1	240	80	63.75	-	-	The ionic liquid catalyst used has strong basic nature as comparable to KOH and is thermally stable. MAG yield of 63.75% achieved at optimum conditions, which is higher in comparison to MgO or hydroxides of potassium, sodium, calcium.	[193]
DES (ATPB: PTSA) In molar ratio of 1:3	5 wt. %	Oleic acid	150	6:1	30	95	27	58	9	Over 85% of mono and di-acyl glycerol are produced and catalyst activity maintained until 5 cycles. Novel study in its application of acid-DES in glycerolysis of oleic acid optimised the reaction to a new level in terms of the greenness of overall reaction and reaction conditions.	[129]

-Not reported or data are not available.

[a](C_{12}:$_0$ - Carbon chain, 12- length and 0- no of double bonds)

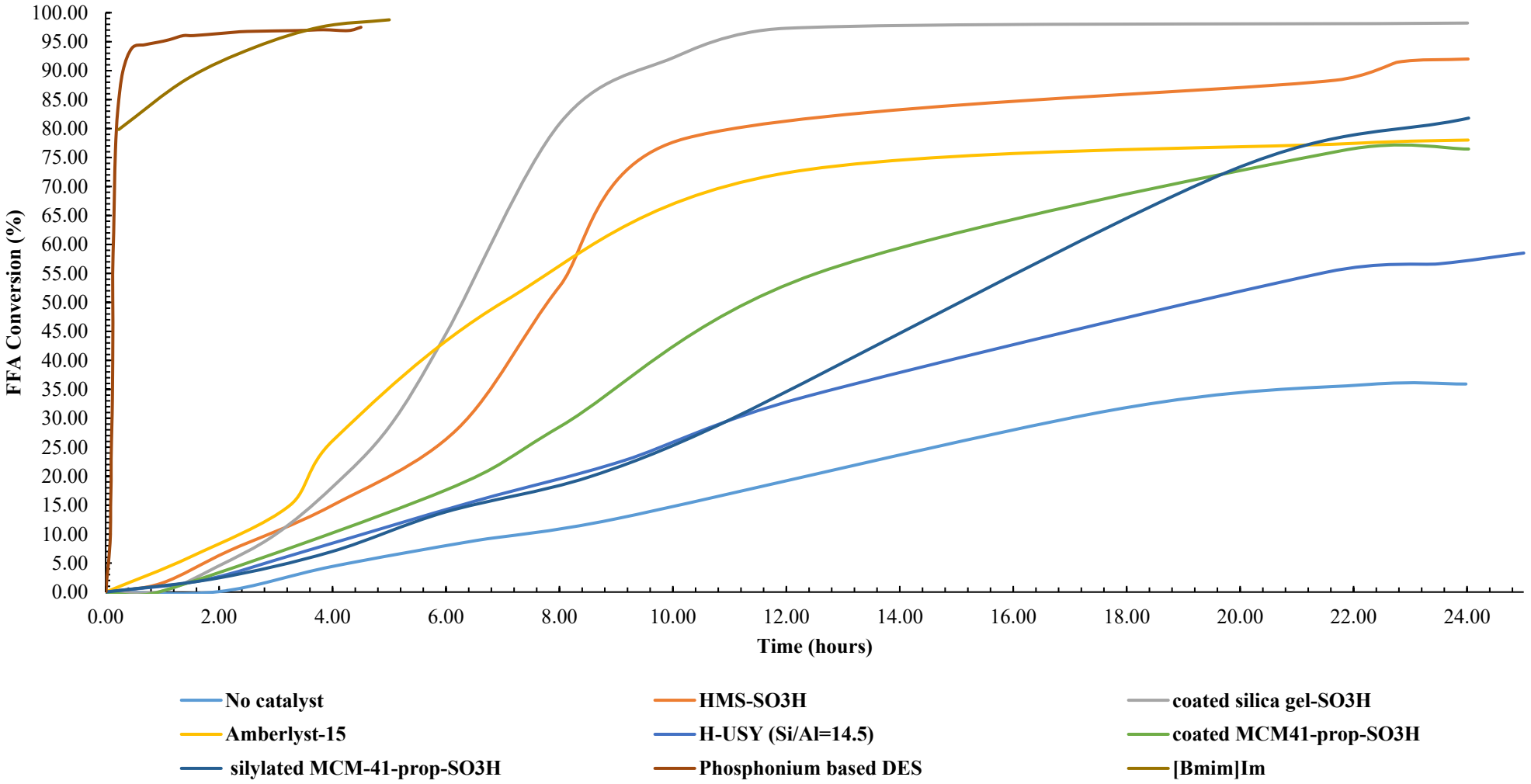


Fig. 11. FFA conversion profile for different heterogeneous and homogeneous catalysts reported in glycerolysis of FFAs. Data adapted from Ref- [128, 177, 184, 192].

3.4 Other catalytic systems

Biodegradable methane sulfonic acid, an excellent Brønsted acid catalyst in the esterification was studied in a microwave assisted glycerolysis of oleic acid [136]. 800 W microwave output power was used to heat the reaction instead of the conventional heating mantle 91% conversion with 0%, 13% and 87% selectivity towards MAG, DAG and TAG respectively, were obtained at the optimum conditions: 191°C, 0.4 bar pressure, 0.3 wt. % of catalyst, 3:1 oleic acid to glycerol molar ration and 104 minutes of reaction time. In comparison to the conventional heating, microwave heating resulted in a reduction in the reaction time (33%) and an increase in the final conversion (50%). This enhancement in reaction rate is attributed to the better and rapid heating provided by the microwave since the radiation was able to directly penetrate into the mixture. In a zinc-acetate catalysed glycerolysis of FFAs, microwave irradiation in comparison with the conventional stirring resulted in a six times faster reaction rate with a similar decrease in energy requirement (203.6 to 35.3 kJ/g). Reductions in initial reaction time (89%) and temperature (47%) were also found [200].

More et al. [201] investigated the effects of ultrasound as the pre-treatment on the glycerolysis of the caprylic acid to the medium-chain triglycerides (MCTs) in the presence of HCl, H_2SO_4 and PTSA with and without silica-gel as adsorbent support. The optimum pretreatment conditions were reported as 60 minutes of irradiation at 50°C at 20kHz, 240W at 60% duty cycle. After this pre-treatment, 1 wt.% catalyst at 4:1 caprylic acid to glycerol molar ratio, 1 wt.% loading of silica gel, 0.33 atm vacuum, 170°C, 400 rpm and 9 hours. They reported 96.6%, 94.4% and 92.7% yield of MCTs in the case of H_2SO_4, HCl and PTSA respectively. The reduction in the reaction time from 24 hours to 9 hours was observed. Mohod et al, [196], also investigated the effect of ultrasonication (US), as a means of agitation, in the glycerolysis of lauric acid, with H_2SO_4 as homogeneous catalyst and $ZnCl_2$ as heterogeneous catalyst. The results for conventional stirring are listed in Table 4. Two configurations were studied i.e., the US-longitudinal horn and US-bath with operating conditions and catalyst loading remaining similar to that of conventional stirred reactor. The reduction in the reaction time to 270 minutes for both catalysts types was obtained. With the US-longitudinal horn, as a means of agitation, 72.3% and 77.5% conversions were obtained for $ZnCl_2$ and H_2SO_4, respectively. While these numbers drop slightly in case of US-bath operated reactor. This is due to the placement/geometry of transducers in the two configurations, in the case of the longitudinal horn, sonication is done more effectively as the transducer is extended into the mixture, while for US-bath, and the operation is done from the periphery. Operating energy consumption for US-longitudinal, US-bath and conventional stirring per unit reduction in acid value was calculated as 15.4 MJ/mg, 16.8 MJ/mg and 16.85 MJ/mg, respectively. However, no reporting of yield or selectivity was done, which could have furthered the analysis. Similar intensification strategy i.e., ultrasound or sol-gel based glycerol adsorption, aforementioned studies, could be applied to glycerolysis of FFAs, for analysis.

Novel use of a DES (ChCl-Gly) with a heterogeneous catalyst (Amberlyst-15 beads) has been investigated recently for the esterification of lactic acid with ethanol for ethyl lactate production, in the pharmaceutical based research area [202]. An increase from 33.8% to 69.3% in the yield of ethyl lactate. The work showed the scope of the typical hybrid catalyst systems, which is capable of overcoming various limitations in the esterification reaction. Similar investigations for glycerolysis of FFAs in biodiesel-research area have not been done and remains as an opportunity.

Glycerolysis in the supercritical reaction conditions is also an attractive alternative to the conventional catalyst systems discussed earlier. Whenever any mixture, compound or element has pressure (P_c) and temperature (T_c) above its critical values, it loses the distinction between liquid/gas phases, its density changes and it behaves as a supercritical fluid [203]. It can then dissolve materials and permeate through solids. SC-CO_2 was used in the lipase-catalysed glycerolysis reactions [204, 205] owing to its relatively low critical parameters and low toxicity. Common fluids reported in literature, with their supercritical conditions (P_c, T_c, ρ_c) are H_2O (22.12, 374.3, 348), CO_2 (7.3, 31.3, 469), CH_3OH (8.09, 239, 272) and C_3H_6O (4.70, 235, 278); in MPa, ℃ and g/L respectively [203].

One important factor while applying supercritical conditions is the stability (at high T and P) of reactants and products as both of them should not degrade under these conditions [206]. One study concluded that fats, oils and FAMEs themselves get partially decomposed at high temperatures and high pressures, especially FAMEs (>330℃) where isomerisation to cis- and trans- isomers takes places [207].

Tai et al [208] studied the lipase-catalysed esterification of glycerol and palmitic acid in acetone as a solvent, with CO_2 as the co-solvent at 65-85 bar and 40-60℃. The reported optimum conditions from the investigation were 85 bar at 50℃ and 25% w/w enzyme (Novozym 435), leading to 77% palmitic acid conversion. In this system, the gas-expanded solvent system, SC-CO_2 added to acetone, reduced the reaction time to 5 h from 24 h. These advantages are due to alterations in the physicochemical properties such as dielectric constant, H-bonding and viscosity of the solvent [209]. However, there is a significant increase in the cost owing to SC-CO_2 in the reaction.

In the glycerolysis of FFAs, a process intensification [133] study by Chuah et al., concluded that microwave and ultra-sonication techniques are still not completely viable for industrial adoption but that hydrodynamic cavitation performs more efficiently in terms of yield, reaction time and energy consumption. Recorded patents cover a number of tailored, glycerolysis reactants and products. These are listed in Table 5. Kochar and Bhatnagar 1962 [210], reported CO_2-catalysed glycerolysis of fats and oils. With aqueous CO_2 in the reaction mixture acting as a catalyst, MAG yield of up to 82.5% was reported in the case of castor oil by the investigators. No such study reporting using only CO_2 as the catalyst in the glycerolysis was found in the literature and thus further investigation to check the validity of their results is required.

Table 5
Granted Patents since 2010 in the field of glycerolysis.

Year	Patentee and assignee	Remarks	Ref
2010	Allan Donald Roden, Jeremy Butz	Base catalysed glycerolysis at 204 ℃ for reducing FFAs concentration in waste vegetable oil. 1:4 w/w ratio of glycerol to (50%) caustic solution in 1L of WVO.	US20100175312A1
2013	Ma Chuanguo et al. (Henan University of Technology)	Lipase glycerolysis of high acid value degummed rice bran oil.	CN102268464B
2013	Deng Zeyuan et al. (Nanchang University)	Immobilised lipase (Lipozyme RMIM) catalysed glycerolysis of deodorised fraction from tea seed oil by employing molecular sieves and mild reaction condition.	CN102342331B
2014	Guan Youyun et al. (Henan Jiuda Industrial Co., Ltd.)	Process optimisation for two-step biodiesel production process, Reactor I glycerolysis and Reactor II transesterification, are connected serially.	CN203890322U
2014	Wang Yonghua et al. (South China University of Technology)	Immobilised lipase (Lipase Tl) is used in partial glycerolysis reaction under a 10~500 Pa vacuum for 2-6 hours at 75-95 ℃ after which centrifugation is done. Re-esterification with glycerol is done for edible oils (palm, soybean etc.)	CN103060394B
2015	Coon Lo et al. (Sime Darby Berhad, Malaysia)	Di-acyl glycerol enriched-oil targeted immobilised lipase glycerolysis reaction. Lipase is supported on hydrophilic siliceous material. Patent more suitable for food processing engineering.	JP5782130B2
2017	Sanjeev Agarwal (Technochem Co)	A feedback loop scheme, specialising in FFAs treatment in an oil involving de-aeration, pre-distillation, steam-distillation, condensation and glycerolysis in a continuous feedback loop. Pre-treatment process intensification is done and glycerolysis is thermally-auto catalysed.	US20160152924A1
2017	Rongsheng Ruan et al. (China Agricultural University, University of Minnesota)	Auto-catalysed high temperature glycerolysis is a part of the multi-step process in producing biodiesel from scum.	US9745530B2
2017	Michael Phillip Doyle and Glenn Richards	Heterogeneous catalyst placed in fluidized-bed multiple-reactor, based glycerolysis of feedstock (2-100% FFA) in a heating vessel with 1.2:1 Gly to oil (w/w) at 196℃. Calcined catalyst is a mix of 90% silica, 18% ZnO powder and ~ 2.3% CuO.	WO2018102793A1
2018	David A. Slade et al. (REG Seneca LLC)	High temperature auto-glycerolysis is part of two-step multi-feedstock biodiesel production process.	US9909077B2
2018	Wang Yonghua et al. (South China University of Technology)	Lipase (Lipozyme Rm) catalysed glycerolysis of grease, in a configuration preferring diglycerides production up to 10 circulations of grease.	CN104830920B
2019	Ana Luísa Dominguez De Matos et al. (Resiway-Solucoes Sustentaveis Lda)	Physical steps like coarse filtration, decantation and centrifugation are employed in addition to glycerolysis at high temperature.	EP3347338B1

4 Conclusion and future trends

For biodiesel to contribute to the renewable energy sector by the mid-century, biodiesel production has to be a market competitive with the conventional diesel. One way to do so is to increase the process efficiency and economics by the process intensification for example by utilising by-product crude glycerol. To maintain sustainability in terms of feedstock flexibility, the biodiesel industry needs to switch to non-edible sources of lipids or oils. This can be done by utilising crude glycerol in-situ for the pre-treatment of non-edible low-grade feedstock such as waste cooking oil, by glycerolysis. With the above considerations, it is seemingly necessary to have a review dedicated to the glycerolysis of high FFAs feedstock. To the best of the authors' knowledge, the work presented here for the first time reviews glycerolysis of the FFAs present in the low-grade non-edible feedstock, in the context of biodiesel production.

For glycerolysis, the conventional path requires excessive energy input, making the whole in-situ glycerol valorisation uneconomical. The behaviour of reactants and products during these transformations is complex and require a better understanding. Glycerol is a bulky, thermally stable and weak nucleophilic attacker in the esterification reaction, implying the need for a suitable catalyst to enhance the reaction. It is observed that in the case of heterogeneous and homogenous catalysts: dispersibility, thermal stability, the acidic strength and hydrophobicity of the catalyst, are the key parameters that affect the activation energy, reaction rate and product yield. Most of the studies reported in the literature have used pure glycerol and pure FFAs, however, at the industrial levels, crude glycerol and waste oils are to be employed. This creates an ambiguity towards the reported results since the very composition of the reactants is different. It has been shown in this work that glycerol purity affects the glycerolysis reaction considerably. Similarly, any deviations from the pure FFAs in the glycerolysis reaction would surely produce differing results. For example, in the application DES, oleic acid and VODD has been reported under the homogenous catalysis. For glycerolysis of these two with pure glycerol, using the same catalyst dosage, one can see the difference in the operating conditions especially reaction temperature and time, in addition to a drop in conversion. Other than this all other parameters have been well investigated and have reached optimum values through the research based development and verification by various investigators.

For enzymatic catalysts, lipase sensitivity towards impurities, in addition to higher costs, poses challenges in upscaling them to an industrial level. Techniques such as bio-silicification of lipases should be focused on to improve lipase stability. Green solvents such as Choline based DES have also proved to be a better solvent in lipase-catalysed reactions. While their use was well researched and reported, the use of strong acids and strong bases in homogeneous catalysis should be avoided to reduce water usage in downstream purification techniques.

In accordance with green chemistry principles, the best performing catalyst systems such as metal derivatives, ionic liquids, heteropolyacids and heterogeneous catalysts like Amberlyst-15, mesoporous silica and hydrotalcite, are not entirely environmentally benign. However, deep eutectic solvents, emerging green solvents, were successful in the glycerolysis of FFAs, performing at par with the best-known catalysts. Advantages such as ease of preparation, low cost, greenness in their production, operation and disposal, are unique to this class of homogeneous catalysts. Over 95% FFA conversion has been reported in the glycerolysis of the oleic acid at 150°C in 30 minutes, however, the monoglycerides selectivity (27%) is way lower in comparison to other catalysts. This opens up a research gap and should be investigated in future studies. Similarly, in-situ application of fatty soaps produced during FAMEs production,

as a catalyst in glycerolysis also carries potential. Catalyst recyclability in this system has been remarkable and requires more investigations. A hybrid (homo-heterogeneous) catalyst system, is also an anticipative alternative to an individual catalyst system, with the potential to combine the advantages of both types of catalyst. In the case of supercritical fluids, apart from CO_2, other fluids make the process very energy-intensive.

Almost all the work reported in the literature studied glycerolysis in a batch reactor. Other comparative reactor technologies such as continuous stirred type reactor and microchannel reactors shall be considered as well. In process intensification through enhanced mixing techniques, ultrasonication, hydrodynamic cavitation and microwave irradiation display significant advantages but are energy-intensive as compared to conventional heating and mechanical stirring, thus requiring more feasibility studies in the future. Though there have been progressive research studies in the field of glycerolysis reaction, an industrially accomplished and environmentally benign process still is not available. No hybrid catalyst systems have been hitherto reported in literature specific to the glycerolysis in biodiesel area. Future studies should also focus on developing the glycerolysis process by improving on catalytic system, to make reaction conditions milder, and on process intensification through novel reactor design and optimisation studies. However, studies addressing the issues of economic feasibility must be done before considering the relevance of any process.

5 Acknowledgement

We acknowledge the New Zealand Government through the Ministry of Foreign Affairs and Trade (MFAT) for providing New Zealand Development Scholarships.

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