Journal of Industrial and Engineering Chemistry

Review of biodiesel production by the esterification of wastewater containing Fats Oils and grease (FOGs)

--Manuscript Draft--

Manuscript Number:	JIEC-D-21-02689R2
Article Type:	Review Article
Section/Category:	Catalyst
Keywords:	Fats Oils and Grease (FOGs); Esterification; Free fatty acid; methyl ester
Corresponding Author:	Katherine Deborah Huddersman De Montfort University City Campus: De Montfort University Leicester, -- State or Province -- UNITED KINGDOM
First Author:	Katherine Deborah Huddersman
Order of Authors:	Katherine Deborah Huddersman
	Rawaz Ahmed, Ph.D
Abstract:	A promising solution for the near future is the substitution of non-renewable fossil fuels with a sustainable liquid feedstock for biofuel (biodiesel) production. The cost of conventional biodiesel production is higher than that of petroleum-based diesel production since it is produced mostly from expensive high-quality virgin oil. 70–80% of the overall biodiesel production cost is associated with the cost of raw materials. Brown grease (with free fatty acid levels > 15%) is created from rendered trap waste and is known as Fats, Oils, and Greases (FOGs). It is a potential source of biodiesel feedstocks and is available at no cost. Many researchers are interested in using low-cost high Free Fatty Acid (FFA) oils as the feedstock for biodiesel production. This paper reviews the effect of feedstock pre-treatment and process parameters on the conversion of FOGs-wastewater to biodiesel by esterification, including alcohol to oil molar ratio, reaction temperature, reaction time, catalyst amount.
Response to Reviewers:	Reviewer comments Reviewer #1: This paper reviews the potential biodiesel production by esterification of wastewater containing Fats Oils and grease (FOGs) and investigated the effect of feedstock pre-treatment and process parameters by esterification, including alcohol to oil molar ratio, reaction temperature, reaction time, catalyst amount. Some important point from previous comment has been addressed by the author. However, author has to consider other comments before considering for publication. 1. Amberlyst catalysts in esterification process has been considered in this paper but more detail information related to operating parameters is necessary and included in Table 3 especially for Amberlyst-15 type as frequently used. The bottom rows of Table 3 have been amended to include a number of Amberlyst catalytic reaction details (Page 13) and further discussion is included in Section 2 page 15. The Amberlyst catalyst and parameters also has been further discussed in section 5 page 23. These sections have been highlighted in yellow. 2. Better to draw carbonyl group in Figure 2 as presented in Figure 1 (O-C=O) instead of -OOC. The carbonyl group of figure 2 has been re-drawn in the same style as figure 1. 3. More important things is the FFAs content in FOGs is around 15% so only few biodiesel products can be expected and huge number of triglyceride (around 85%) is necessary to considered as main process of biodiesel production from FOGs as feedstock using transesterification. Instead, hydrolysis reaction pathway can be considered to convert triglyceride into free fatty acid and thus, esterification process can be totally selected as a main process of biodiesel production. So we recommend the author to consider either esterification-transesterification or hydrolysis-esterification reactions pathway for FOGs-to-biodiesel conversion. A significant section on the describing both esterification-transesterification as well as

the hydrolysis-esterification reactions for FOGs conversion to biodiesel has been included in Section 3 and highlighted in green.

4. By considering the comment No. 1 and 3 then it gives additional information and clearly understanding of the main idea of this paper. Otherwise, this paper review still not enough for comprehensive reviews and only considered as mini review due to the less contents and figures.

We believe that we have fully answered both comments 1 and 3 and trust that the reviewer considers the paper suitable as a full review.

Reviewer #5: The revised manuscript has addressed most of my comments and adopted most of my suggestions. By explicitly describing and summarizing the previous findings, the manuscript has substantially improved after the revision. There are some amendments needed.

1. The formats of table and graphs are not regular. For example, the font used in the table is not uniform in Table3 (Page11). And there lacks consistent format in one graph (including the font size, format, graph size). Other than that, the formats of the whole manuscript should be checked.
The font size throughout the paper has been checked especially for Table 3.

2. please check and correct the errors in the table (Page16, Line 11 and 34-35 2g LA).
The errors have been corrected in Table 4 pages 21-22

3. Scheme 3 uses the image of the referenced paper directly, which is not recommended. Therefore, the authors are suggested to draw their own mechanism diagrams.
Scheme 3 has been redrawn.

DE MONTFORT
UNIVERSITY
LEICESTER

November, 18th 2021

Attn: Editor-in-chief: Journal of Industrial and Engineering Chemistry

Thank you for inviting us to submit our work to Journal of Industrial and Engineering Chemistry. Please, find our paper entitled **“Review of biodiesel production by the esterification of wastewater containing Fats Oils and grease (FOGs)",** authors Rawaz Ahmed and Katherine Huddersman.

The submission is original, not under consideration for publication elsewhere. All the authors are aware of the submission and agree to its publication in Journal of Industrial and Engineering Chemistry. This review differs from a previous review in your journal which was focussed on the esterification of short chain carboxylic acids with alcohols which is considerably easier than the esterification of long chain fatty acids, such as, stearic acid.

The purpose of our review is to reduce Free Fatty Acids (FFAs) in Fats, Oils and Grease (FOGs). This review for the first time gives an overview on the reaction conditions for esterification of high content of FFAs from wastewater containing FOGs, which is important as a low cost feedstock for the production of renewable energy as biodiesel. The benefit of this review is that firstly it shows the potential of using and recycling a low cost feedstock which causes severe environmental pollution, and blockage of sewers in developed countries such as the UK and USA. Secondly, fatty acid methyl esters (FAMEs) /biodiesel the outcome of esterification is a renewable energy with low carbon dioxide emission, zero or lower sulphur content and lower particulate matter emission especially of concern in the transportation sector. Nowadays, the global use of biodiesel as a fuel is approximated at 10% and the aim is to increase this as a cleaner alternative energy for fossil fuel and traditional petroleum energy. This review also highlights the critical process parameters which optimise the esterification reaction of the high FFA content of the waste feedstock FOGs making the production of biodiesel from FOGs possible.

Yours faithfully
Katherine Huddersman
Professor of Environmental Chemistry
Faculty of Health and Life Sciences
De Montfort University
The Gateway, Leicester LE1 9BH
England
00 44 (0)1162 577134
huddzeo1@dmu.ac.uk

Faculty of Health and Life Sciences, The Gateway, Leicester, LE1 9BH
Tel (0116) 255 1551 / **Fax** (0116) 257 7533 / **ISDN** (0116) 275 5069 / **Email via the web** www.dmu.ac.uk/enquiry

*Graphical Abstract

Review of biodiesel production by the esterification of wastewater containing Fats Oils and grease (FOGs)

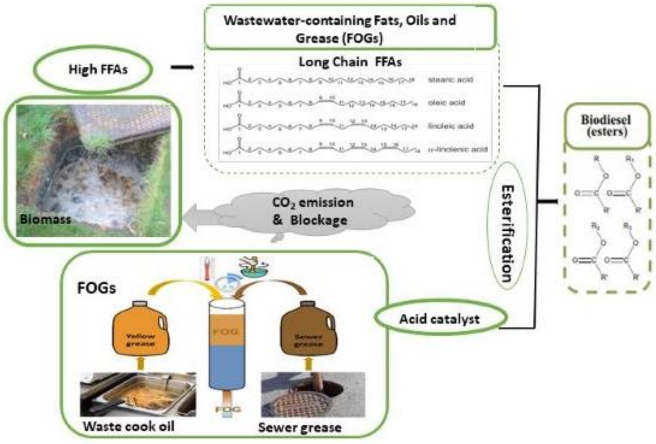
Rawaz Ahmed and Katherine Huddersman

Faculty of health and life science at De Montfort University/Leicester
Email: huddzeo1@dmu.ac.uk and rawaz.ahmed2@dmu.ac.uk

Abstract

A promising solution for the near future is the substitution of non-renewable fossil fuels with a sustainable liquid feedstock for biofuel (biodiesel) production. The cost of conventional biodiesel production is higher than that of petroleum-based diesel production since it is produced mostly from expensive high-quality virgin oil. 70–80% of the overall biodiesel production cost is associated with the cost of raw materials. Brown grease (with free fatty acid levels > 15%) **is** created from rendered trap waste and is known as Fats, Oils, and Grease (FOG) It is a potential source of biodiesel feedstocks and is available at no cost. Many researchers are interested in using low-cost high Free Fatty Acid (FFA) oils as the feedstock for biodiesel production.

This paper reviews the effect of feedstock pre-treatment and process parameters on the conversion of FOGs-wastewater to biodiesel by esterification, including alcohol to oil molar ratio, reaction temperature, reaction time, catalyst amount.



Sustainable biodiesel from Wastewater containing FOGs

Keywords: *Fats Oils and Grease (FOGs); Esterification; Free fatty acid; methyl ester*

Highlights

- Literature review on the esterification/transesterification catalytic processes in biodiesel production
- Highlighting the use of Fats, Oils, and Greases (FOGs) from wastewater.
- Reduction of high Free Fatty Acid (FFA) content of FOGs by esterification to methyl/ethyl ester
- Evaluation of the esterification reaction conditions, such as temperature, time, types of catalyst, and alcohol.

Review of biodiesel production by the esterification of wastewater containing Fats Oils and grease (FOGs)

Rawaz Ahmed and Katherine Huddersman

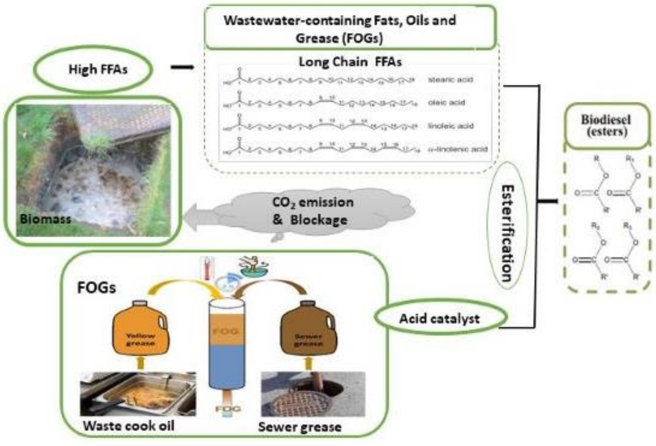
Faculty of health and life science at De Montfort University/Leicester

Email: huddzeo1@dmu.ac.uk and rawaz.ahmed2@dmu.ac.uk

Abstract

A promising solution for the near future is the substitution of non-renewable fossil fuels with a sustainable liquid feedstock for biofuel (biodiesel) production. The cost of conventional biodiesel production is higher than that of petroleum-based diesel production since it is produced mostly from expensive high-quality virgin oil. 70–80% of the overall biodiesel production cost is associated with the cost of raw materials. Brown grease (with free fatty acid levels > 15%) is created from rendered trap waste and is known as Fats, Oils, and Greases (FOGs). It is a potential source of biodiesel feedstocks and is available at no cost. Many researchers are interested in using low-cost high Free Fatty Acid (FFA) oils as the feedstock for biodiesel production.

This paper reviews the effect of feedstock pre-treatment and process parameters on the conversion of FOGs-wastewater to biodiesel by esterification, including alcohol to oil molar ratio, reaction temperature, reaction time, catalyst amount.



Sustainable biodiesel from Wastewater containing FOGs

Keywords: *Fats Oils and Grease (FOGs); Esterification; Free fatty acid; methyl ester*

Highlights

- Literature review on the esterification/transesterification catalytic processes in biodiesel production
- Highlighting the use of Fats, Oils, and Greases (FOGs) from wastewater.
- Reduction of high Free Fatty Acid (FFA) content of FOGs by esterification to methyl/ethyl ester
- Evaluation of the esterification reaction conditions, such as temperature, time, types of catalyst, and alcohol.

Contents

1. Introduction

Bio-fuels are gaining worldwide attention as an alternative fuel option replacing the usage of the mineral diesel derived from conventional fossil sources. The production of fuels from renewable biomass replacing the currently used traditional sources [1]. Among liquid renewable energy, biodiesel has been identified as able to be used directly in a diesel engine without requiring any modification [2]. Biodiesel is a fuel derived from edible and non-edible oils made by chemically reacting lipids such as animal fat (tallow), soybean oil, or some other vegetable oil with an alcohol producing a methyl, ethyl, or propyl ester [3, 4]. It is well known that the major cost involved in biodiesel production technology is dependent upon the used feedstock as virgin oil. The non-edible oil such as FOG is a lipid-rich waste in wastwater can be considered as a potential feedstock owing to its low cost and abundant availability [1,5,6]. Among the different renewable liquid feedstock's that have been studied, wastewater containing Fats, Oils, and Greases (FOGs) is the least explored one for biodiesel production. A recent analysis of brown grease (discharged into the sewer system) contained 60 % FOGs, 25 % water, and 15 % biosolids by mass [7]. Direct discharge of FOG clogs up the pipes and disturbs the plumbing of individual housing resulting in property flooding. The serious consequences of sewer pipes blocking results in sanitary sewer overflows (SSO) which further causes unhealthy environmental and hygiene deteriorations. Recently, the major causes of sewer blocks were attributed to FOG in many counties like US (50%), Malaysia (70%) and UK (50%), with an estimated annual cost of about US$ 25 billions for removal of this sewer blockage in US alone. Thus, FOG deposition is a precedent alarm globally which requires an effective management. Beyond a few measures, no sustainably effective managements have so far been devised. Hence, this issue needs to be adressed before it gets even bigger because of growing population and eventual urbanization [8].

One of the promising solutions to these problems is the challenges to developing eco-friendly, lower-environmental impact and more sustainable technology to convert FOGs found in wastewater into renewable energy (biodiesel). Thus, the coversion of FOGs to biodeisel production via transesterification/esterification reactions (See Fig.1 and Fig.2) also has been successfully investigated [9][10].

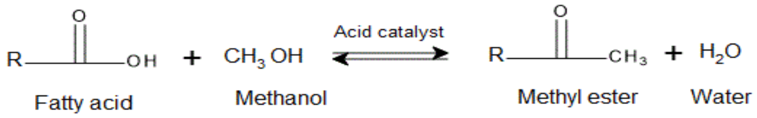


Figure 1 : Esterification reaction for biodiesel synthesis [9].

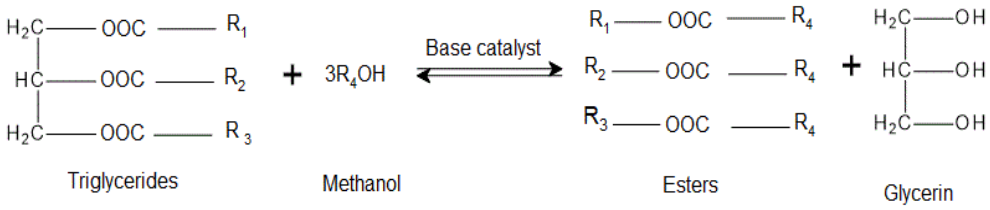


Figure 2: Transesterification reaction for biodiesel synthesis [9].

Where R, R_1, R_2, R_3 and R_4 denotes any hydrocarbon chain. Since both reactions are equilibrium reactions, the molar relation of alcohol/oil should be over the stoichiometric amount to be able to achieve a good conversion of the FFA as well as of the triglyceride (TG).

Fats, oils and greases (FOGs) composition varies according to the country, region and different sources. For example, FOG obtained from restaurants contains about 15% FFAs, which entirely depends upon the source of FOG. Based on FFAs content, FOG can be classified into two main groups, namely yellow grease (less than 15% FFAs) and brown grease (above 15% FFAs) [11]. For instance, about 8% FFAs content was detected in grease interceptors located in the canteen of National University of Singapore [12]. Suto et al. [13] analyzed 27 different restaurant grease samples and recorded about 48% of saturated fats, whereas it was not determined in the dewatered restaurant grease anayzed by Parry et al. [14]. Analytical study of the fatty acid, triglyceride (TAG) and tocopherol composition of oil extract from the fruit of Algerian tree Argania spinosa found that the oil was found to contain trisaturated (0.47%), disaturated (9.3%), monosaturated (43.95%) and triunsaturated (45.20%) FA. The oil was characterised by a relatively high amount of tocopherols (1027.8 mg/kg). The (γ+β) -tocopherols were the major isomers, with the rest being α- and δ-tocopherols [15]. Thus, the profile and concentration of total fatty acids largely depend upon the sources generating FOG. Table 1 shows the fatty acid profile of different FOG in comparison with other edible feedstocks.

Table 1 : Fatty acid profile of different types of fat, oil and grease (FOG) in comparison to the common edible feedstocks [8].

Fatty acids	Different kind of FOGs							Edible feedstocks			
	FOG		Yellow grease			Brown grease		Corn	Sunflower	Soybean	Rapeseed
Caprylic acid (C8 :0)	nd	0.9	nd	nd	nd	nd	nd	nd	nd	nd	nd
Capric acid (C10 :0)	nd	1.3	nd	nd	nd	nd	nd	nd	nd	nd	nd
Luric acid (C12 :0)	nd	3	nd	nd	nd	nd	nd	nd	nd	nd	nd
Myristic acid (C14 :0)	1.3	8.4	2.43	nd	1.4	1.7	1.66	0.2	0.1	nd	nd
Palmitic acid (C16 :0)	38.3	23.1	23.24	16	37.5	22.8	22.83	13	5.5	11.6	3.49
Palmitoleic acid (C16 :1)	1.2	nd	3.79	nd	3.1	3.1	3.13	nd	0.1	0.3	nd
Stearic acid (C18 :0)	7.2	9.8	12.96	5.21	4.8	12.5	12.54	2.5	4.7	4.2	0.85
Oleic acid (C18 :1)	36.9	36.1	44.32	34.28	36.3	42.4	42.36	30.5	19.5	21.6	64.4
Linoleic acid (C18 :2)	15.1	15.3	6.96	40.76	15.2	12.1	12.09	52.1	68.5	53.7	22.3
Linolenic acid (C18 :3)	nd	nd	0.67	nd	nd	0.8	0.82	1	0.1	7.5	8.23
Arachidic acid (C20 :0)	nd	2.1	nd	nd	nd	nd	nd	0.5	0.3	0.8	nd
Eicosenoic acid (C20 :1)	nd	nd	nd	nd	nd	nd	nd	0.2	0.1	0.3	nd
Benhenic aicd (C22 :0)	nd	nd	nd	nd	nd	nd	nd	nd	0.9	nd	nd
Others	0	0	5.62	3.75	1.7	4.6	4.57	0	0.2	0	0.73
Reference	12	13	11	14	12	11	11	15	15	15	14

nd : non detectable

Esterification is an industrially important process utilized for pharmaceutics, food, flavourings, and biofuels (biodiesel). Esterifying long chain free fatty acid (FFAs) using homogenous acid catalyst is a promising solution to take advantage of high free fatty acid content of FOGs from a wastewater feedstock to obtain a renewable energy i.e., biodiesel [9,16,17]. The traditional transesterification processes using homogeneous base catalysts such as KOH or NaOH are found to be not suitable for processing these types of feedstocks.

This is due to the high free fatty acid (FFA) and moisture content in the FOGs wastewater will cause saponification during the transesterification reaction of Figure 2 and hence, lower the yield of esters. In order to overcome this situation, acid catalysts are used to lower the free fatty acid content by esterification before the transesterification process. Strong acid catalysts which are less susceptible to the influence of free fatty acid can simultaneously esterify and Trans-esterify low quality feedstock's simplifying the biodiesel production from low cost and high FFA content feedstock [18].

Biodiesel or alkyl esters of fatty acids are commonly produced using homogeneous acid catalysts such as H_2SO_4, HCl and H_3PO_4 in the esterification reaction. Homogeneous acid catalysed reactions can produce environmental and corrosion problems. In green technology, heterogeneous acid catalysts were shown to be the best alternative to homogeneous catalysts due to their easy separation of products, recovery and recyclability with less waste emission hence, reducing the environmental impact and process costs [19].

For example in the study of Lee and his colleagues, the conversion of fat, oil and grease (FOG) into fatty acid methyl esters (FAMEs) without pre-treatment of FOG was investigated. A thermally induced process to accomplish simultaneous esterification of free fatty acids (FFAs) and transesterification of lipids was introduced. Despite high contents of impurities in FOG (~14 wt. %), the maximum achievable yield of biodiesel/FAMEs (fatty acid methyl ester) on feedstock mass basis was >86% for 10 s reaction time without removal of impurities prior to the reaction while conventional acid catalysed reaction only produced less than 27.7 % of biodiesel from FOG [20]. Also the most current pablication, Taipabu et al. [21] has fouced on Production of renewable fuels and chemicals from fats, oils, and grease (FOG) using homogeneous and heterogeneous catalysts based on computianla design via both esterification and transesterification reaction. The optimum operating conditions reported that of Est-Design-2 and TransEst-Design-2 are 100 ◦C of reaction temperature at 480 min, and the molar ratio of methanol to oleic acid with 9 :1, and 75 ◦C of reaction temperature at 63 min, and the molar ratio of methanol to triolein with 3.84:1, respectively [21].

In recent times, different heterogeneous catalysts were developed and used for the esterification reaction, optimisation of reaction parameters and these include ZrO_2/SiO_2 catalysts [19], ZrO_2 based solid acid heterogeneous catalysts [22] and zeolite catalysts [23], amberlyst 70 catalyst [24], Amberlyst-15 resin catalyst [25], Amberlyst 46 resin catalyst [26], Amberlyst- 15 ion exchange resin [27], sulfated montmorillonite clay acidic catalyst [28], Sulfated zirconia solid acid catalyst[29], template-assisted mesoporous sulfated zirconia solid acid catalyst [30].

This review focuses on hetrogenous catalysis in the esterification of high free fatty acid lipid feedstock from wastewater containing FOGs and their transformation to biodiesel as a promising solution to achieve renewable energy in near future. Esterification of FFA to alkyl esters in the presence of an acidic catalyst is a route to improving the use of high FFA oils (e.g. some animal and vegetable oils) in biodiesel production. This work aims to review and understand the parameters that affect the conversion of fatty acids reacted with short chain alcohols to achieve better biodiesel yields.

2. Literature review

An extensive literature review has been carried out in order to assess the advantages and disadvantages of the catalytic esterification/transesterification for recalcitrant FOGs wastewater (see Tables 2 and 3). A summary of work performed so far shows that catalyst structure, morphology, texture, optmization reaction parameters such as tepmerature, Catalyst concentration, reaction time, alcohol to substrat molar ratio, type of alcohol have a significant influence on the catalytic activity of biodiesel production from wastewater. Despite a large number of studies carried out on the catalytic esterification of FFAs in FOGs wastewater, there are still a number of drawbacks that hinder industrial application. Therefore, there is a need to develop cheaper more efficient catalysts that are less energy demanding in terms of their process conditions and that have optimal lifetime stability.

Table 2 : Comparison of the performance of homogenous catalysts on waste oil feedstock for biodiesel production

Catalyst	**Feedstocks**	**Transesterification/ esterification reaction conditions**	**Biodiesel yield**	**Cycles**	**Ref.**
H_2SO_4, ferric sulfate co-catalyst ($Fe_2(SO_4)_3$)	Brown grease from wastewater plant	Response Surface Methodology (RSM) was used to evaluate the correlation between the process variable and the response. Optimized conditions were 35 ml MeOH, 1.3 ml H_2SO_4, and reaction time of 120 min.	99.70 %	30 runs	7
H_2SO_4	Fats, Oils, and Grease (FOGs) Without treatment	-Methanol to feedstock molar ratio of 30, and (H_2SO_4 to FOGs feedstock molar ratio of 1.3); - Thermal esterification/transesterification at 240 °C to 350 °C and 10 s reaction time., 10 mL of FOGs, 200 mL of methanol, and 100 mg of silica were used,	> 86%		20
Acid catalyst synthesised using coconut meal residue (CMR)- CMR-DS-SO_3H	Grease Trap wastewater (GTW)	Methanol : oil (molar ratio) (6 :1–16 :1), reaction time (6– 16 h), and (5 %wt.) catalyst loading at 65–70° C. CMR-DS-SO_3H catalyst had high acid density (3.8 mmol/g).	> 80%	4	31
Acidic homogeneous Catalyst HCl	Wastewater treatment plant (WWTP) municipal sludge	Novel direct liquid-liquid lipid extraction used as pre-treatment of feedstock. Compared to standard drying method, direct liquid-liquid lipid extraction resulted with 53% higher lipid and 56% higher biodiesel production.	56%		32
HCl	Wastewater treatment plant (WWTP) municipal sludge (Primary, secondary, blended and stabilised sludge)	The influence of pre-treatment methods (ultrasonic and mechanical disintegration) was tested, but it did not increase significantly the amount of extracted lipid as well as biodiesel yield.	19%	4	33
H_2SO_4	Two type of WWTP sewage sludge obtained from the anaerobic–anoxic–oxic (A^2 /O)	-Methanol-to sludge mass ratio of 10 :1, a temperature of 60 °C, and a H_2SO_4 concentration of 5% (v/v), (from A^2 /O reactor).	96.7% 92.7%		34

	and membrane bioreactor (MBR) processes as lipid	- Methanol-to-sludge mass ratio of 8:1, a temperature of 50 °C, and a H_2SO_4 concentration of 5% (v/v), (from MBRreactor)			
H_2SO_4	Wastewater treatment plant (WWTP) municipal sludge (Primary, secondary, blended and stabilised sludge)	The lipid sample (up to 50 mg), dissolved in 1 mL of hexane. After that, 2 mL of 1% sulfuric acid in methanol was added, heated overnight at 50 ˚C. 5 mL of 5% sodium chloride in water was added and the FAMEs were extracted 2 times with 5 mL of hexane.	87%	2	35
H_2SO_4	WWTO-Municipal wastewater sludges primary and secondary	75 °C, 5% (v/v) H_2SO_4, and 12 :1 methanol to sludge mass ratio.	75%	/	36
H_2SO_4	- WWTP : dried sludge, - WWTP : dewatered primary sludge	-10 g of dried sludge were suspended in 100 mL methanol with 0.25 mL of H_2SO_4 (96%), kept at 65 °C for 7 h.- 150 g of dewatered primary sludge mixed with methanol (300 or 750 mL) and 1.5 mL of sulphuric acid (96%). Kept at 65 °C for 7 h.	60.7% 85%	4	37
A homogeneous base, KOH and acid, H_2SO_4 catalyst	Waste spent coffee grounds (SCG)	Combines simultaneous soxhlet extraction-esterification/transesterification in a single step to produce biodiesel directly from wet SCG, molar ratio of co-solvent methanol to hexane of 1 : 2 and reaction time 30 min, 10 g of wet SCG biomass, 0.75 M of KOH or H_2SO_4 was used as catalyst. Base catalyst showed superior catalytic activity	97%	5	38
H_2SO_4	Fats, oil, and grease (FOG), the main composition of dewatered grease trap waste (GTW)	After Hexane extraction of FOGs, the FOG – ethanol molar ratio was 1 :3, 3 wt. % H_2SO_4 based on the amount of FOG, the reaction temperature was set at 65^{o}C and the stirring speed was kept at 300rpm	96 %		39

Table3 : Comparaison of the performance of heterogeneous catalysts in biodiesel production

Catalyst	**Feedstocks**	**Method of synthesis**	**Transesterification/ esterification reaction conditions**	**Biodiesel yield %**	**Cycles**	**Ref.**
Mo-Mn/γ-Al$_2$O$_3$ bimetallic catalyst containing 15 wt. % MgO	Waste cooking oil (WCO)	Bifunctional heterogeneous catalysts were prepared using a modified wet impregnation method	Methanol to oil molar ratio of 27 :1 and an agitation speed of 500 rpm, 100 °C, 4h.	91.4	8	40
Novel acidic ionic liquid polymer	Fried cooking oil	Copolymerization of acidic ionic liquid oligomers and divinylbenzene (DVB)	Methanol : rapeseed oil 16 :1 molar ratio, temp. 70 °C, 12 h, The optimal amount of the catalyst was 50 mg.	99.0	6	41
Saw dust (used as the heterogeneous nano catalyst)	Waste cooking oil	Chemical activated : dried saw dust is mixed with hot sulphuric acid and stirred until the slurry mixture solidified. - Physical activation : dried saw dust calcinated from 600 ˚C - 1000 ˚C	Esterification by using H_2SO_4. The best yield at : a methanol : oil =8 :1, catalyst (5w/w%), temp.50 ºC, 1.5 h at 600 rpm for chemical activation. The best yield at : a methanol : oil = 12 :1, catalyst (5%), temp. 60 ± 1 ºC, 1.5 h at 600 rpm for physical activation.	Physically activated 65.5, chemically activated ,90		42
Solid base catalysts (K_2O/CaO-ZnO)	Soybean oil	Co-precipitation method and impregnation method	Temp.60 ⁰C, catalyst loading of 2 wt. %, methanol to oil ratio =15 :1, time 4 h. The incorporation of K_2O on the CaO-ZnO catalyst enhanced the catalytic activity due to increased basicity and surface area.	81.08		43
CaO/Fe_3O_4 @SiO_2	Waste sunflower oil	Combination of sol-gel and incipient wetness impregnation methods	Catalyst 6 wt. % ; oil to methanol molar ratio 1 :15 ; Temp. 65°C ; mechanical stirring 500 rpm ; time 5 h.	97	Several batch	44

A nano-magnetic catalyst KF/CaO–Fe_3O_4	Stillingia oil	Facile impregnation method	Reaction is carried out at 65 °C with a methanol/oil molar ratio of 12 :1 and 4 wt. % catalyst, 3 h of reaction time.	95	14	45
CaO powder	Crude Jatropha oil	Calcination–hydration dehydration of Polymesoda erosa shells how does this relate to CaO	Catalyst ratio to oil : 0.02:1 (w/w%) ; reaction time 133.1 min ; oil/ methanol molar ratio 1 :5.15 ; temperature 65°C ; stirring rate 500 rpm	95.8	9	46
Novel Mg/Al/Zn Hydrotalcite/SBA-15	Soybean oil (SBO)	Sol-gel method one pot preparation	The pelletized (0.5–0.8 mm) 1 mL catalyst was sandwiched between glass wool and ceramic beads in an Inconel reactor, reaction temp. Range= (180–300 °C), reaction time of 2 h. oil to methanol ratio= (1 :5–1 :30).	90	> 200 h TOS	47
CaO, Li- CaO catalyst, $Fe_2(SO_4)_3$ solid acid, CaO +$Fe_2(SO_4)_3$ mix Li- CaO +$Fe_2(SO_4)_3$	-Jatropha curcas oil - - rapeseed oil	CaO was prepared by decomposing pulverized $CaCO_3$ at 960 ˚C for 3½ h. Lithium doped calcium oxide (Li-CaO) was prepared by the incipient wetness or impregnation method.	Temp. 60 ° C, 3 h time, molar ratio of alcohol to oil = 6 :1, 5 wt. % catalyst (based on the amount of oil), 300 rpm. Single step transesterification /esterification performed over mixed acid-base catalyst (CaO : $Fe_2(SO_4)_3$ = 3 :1 & Li- CaO : $Fe_2(SO_4)_3$ = 3 :1).	93.3 CaO/$Fe_2(SO_4)_3$ 96 Li /CaO/ $Fe_2(SO_4)_3$	3	48
Iron (II) doped ZnO nano-catalyst	Castor oil	Impregnation method	50 min at 55 °C with 14 wt % catalyst loading and 12 :1 methanol/oil ratio.	91		49
CaO derived from, $CaCO_3$, -Ca $(OH)_2$, -limestone	Palm oil	Thermal processing in a muffle furnace at 900º C	Esterification : A 800 ml cooking oil was mixed with 10 ml H_2SO_4, methanol to FFA molar ratio 40 :1, heated to 60 °C, 600 rpm, time 2 h. Transesterification : 100 ml of cooking oil filled into ultrasonic reactor. Mole ratio methanol to oil 9 :1 and catalyst loading 2.6 wt. %, for 40 minute.	85.15% for Ca $(OH)_2$; and 78.71% for $CaCO_3$ catalyst.	NA	50

3. Lipid extraction from Biodiesel Feedstock

Brown grease obtained from a wastewater plant was heated to separate biosolids, debris, and oil from the wastewater by decantation. Alternatively, the crude brown grease was screened to remove large debris, melted to separate the water from the biosolids and most of the biosolids, which settled to the bottom, and the wastewater screened again to remove any remaining biosolids. This brown grease still contained significant amounts of water, which was removed by azeotropic distillation with toluene, so that the toluene content of the brown grease generally did not exceed 5wt. % [7].

A novel direct liquid-liquid lipid extraction method for both sewage and petrochemical industry WWTP sludge's was investigated (see Fig 3). This method did not require expensive sludge dewatering/drying steps compared to the standard drying procedure involved in lipid extraction. Higher lipid and biodiesel yields resulted for petrochemical industry WWTP sludge samples than that obtained by standard drying method. From an economy point of view, liquid- liquid lipid extraction method may be preferred as it eliminates dewatering/drying steps, contributing to 50% of the whole biodiesel production cost [32].

The study explored an alternative method compared to common sludge drying methods (standard method) for lipid extraction, which was called the direct sequential liquid–liquid extraction, in a batch mixer–settler reactor at room temperature, using hexane as a solvent. The optimised direct liquid–liquid extraction of lipids from municipal sewage sludge for biodiesel production, recovered 91% of the lipid fraction from the primary sludge after three extractions. The optimised extraction gave slightly higher lipid content (27w/w%, dry sludge) than the standard method (25%, dry sludge). The proposed alternative, liquid–liquid extraction using hexane, is feasible and compares well with the classical methods [51].

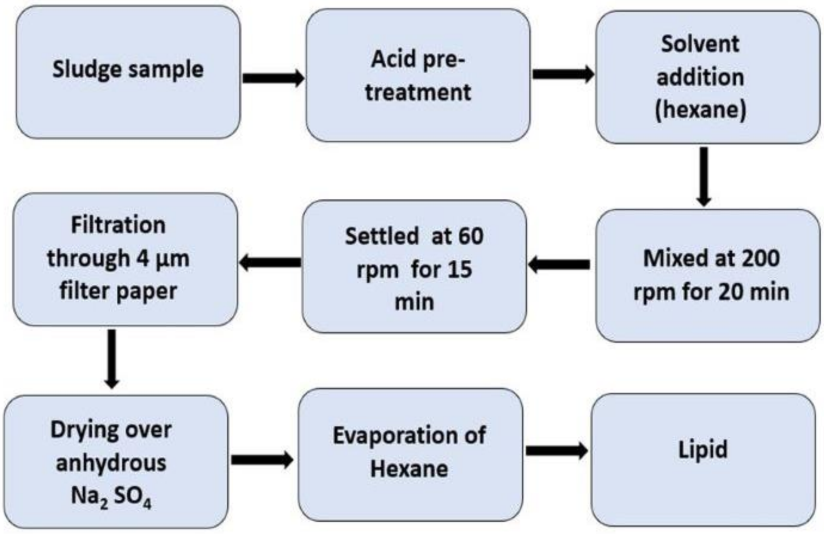


Figure 3 : Direct liquid-liquid lipid extraction of sludge wastewater [32, 51].

Different organic solvents have been used for the simple extraction of FOGs from dewatered grease trap waste (GTW). The raw GTW is first dried in an oven at 110 °C for 24h to 48h until the moisture content of the sample dropped below 5w/w%. FOGs were extracted using different solvents such as ; hexane (HEX), diethyl ether (DEE), and a mixture of hexane - diethyl ether (HEX-DEE). The results showed that the extraction yield increased using the extraction solvent in the following order : DEE > HEX-DEE > HEX. Approximately 88% of FOGs were extracted after two -three extractions [39] . Another study used 200 ml of a mixture of co-solvent methanol, hexane and acetone with different ratios, at 50 °C for 4h to extract lipid from scum, primary and secondary sludge (dry sludge), with sequential extractions using recovered solvent fraction performed three times. It was also found in the study that the neutral lipid was dominant in scum sludge and the maximum lipid yield accounted for one-third of the dried scum sludge when the extraction was performed with the co-solvent (methanol, hexane) containing a high percentage of hexane (60%). Scum sludge achieved the greatest lipid yield (33.3%) compared with primary and secondary sludge which managed to achieve yields of 27.0% and 16.9%, respectively [52].

A solvent-free approach to extract the lipid fraction from sewer grease (SG) for biodiesel production had been used. Waste cooking oil (WCO) was used as the solvent for sewer grease extraction, under optimal condition which were as follows ; 3.2:1 WCO-SG ratio (wt. /wt. %), 70 °C and 240 min. Lipid extraction efficiency from sewer grease was over 90% after two to three sequential extractions reusing WCO solvent [53].

4. Heterogeneous catalysis in the Esterification of fatty acids

The emphasis on environmental protection, as industrial and economic growth gave birth too many forms of pollution threatening human health and earth ecosystems, resulted in the growth of environmental catalysis. Recently, focus has been centered on the use of heterogeneous catalysts due to their properties ; low cost, recoverable and reuse able, easily available, less waste generation, as well as generally environmentally friendly. Esterification of fatty acids with short chain alcohols is very important as this can contribute to the production of biodiesel. Notably, acidic ion exchange resin Amberlyst-15, Amberlyst- 46, Amberlyst-70, Amberlyst-35 and Amberlyst-16 which is an effective, cheaper, and green heterogeneous catalyst and have been widely established for esterfication of free fatty acid. Ion exchange Amberlyst types bead catalyst have high activity towared esterifcation process, due to having high surface area, macroporous pore size active surface (SO_3H) group exhibiting strong acid functionality, allowing good accessbilty of the substrates and contact with the protonated group, [24,25,27,26, 54,55,56, 57]. For example, Boz N. et al.[54] used Amberlyst 15 and modified Amberlyst 15 with optimum reaction conditons of methanol to oil molar ratio 12 :1, 65°C ,3 wt. % catalyst and reaction duration of 540 min to give the highest biodiesel yield of (78 ± 3.39%). Zhang et al. [55] used Amberlyst-15/Poly (vinyl alcohol) membrane as a bifunctional catalyst for obtained high quality biodiesel (98% conversion) from waste cooking oils (WCO), with molar ratio of alcohol to oil 2.5 :1, 15wt. % of catalyst, 65 °C and 120min of reaction time [55]. He proposed the mechanism of esterficaiton reaction over Amberlyst-15 which is discussed in section 6. Also Petechoongsakul et al.[56] observed highest esterification conversion of free fatty acid from waste food oil (WFO) approximately (99.87%) over Amberlyst-15, with molar ratio of alcohol to WFO 4.0 :1, 5wt% of catalyst, using a high reaction temperture of 247-273 °C [56]. Table 4 describes a variety of different types of heterogeneous catalysts and reaction conditions which have been used in the esterification of long chain acids.

Table 4 Heterogeneous catalysis for the esterification of long chain fatty acid (model compounds)

Long chain fatty acid	Catalyst	Reaction conditions	Conversion%	Ref.
Stearic acid	Mesoporous ZrO_2/SiO_2 catalysts prepared with cationic (CTAB) and non-ionic surfactants.	0.4 g of catalyst, reaction time 3hr, ethanol/stearic acid molar ratio of 120 :1, reaction temp. 120 ˚C	76.9% which reduced to 72.5%after five cycles,	19
Stearic acid	Iron Exchanged Montmorillonite (Fe-MMT K10) catalyst	Stearic acid was heated with either ethanol or methanol at 80 ^{o}C for 3 hrs with 2 g of stearic acid in 100 ml of alcohol and 600 mg of solid catalyst.	68%, with ethanol 78% with methanol	58
Stearic acid	PA/NaY (PA = organophosphonic acid, NaY = NaY molecular sieve) catalyst	2.0 g catalyst, reaction time : 4 h, molar ratio of alcohol to acid : 4 :1 and temp : 95 and 100 ˚C.	69.10%	59
Oleic acid	Co-Ni-Pt/ FAU-type zeolites catalyst	Ethanol to oleic acid molar ratio 6 :1 (50ml = 44.75 g); max Temp 70 °C, reaction time 1.5-2 h, batch and continuous esterification	93% for batch and 89% for continuous process	23
-Lauric acid -Palm fatty acid distillate (PFAD)	Ammonium ferric sulphate-calcium silicate AFS-CS catalyst	Methanol to lauric acid (2g LA) or Palm fatty acid distillate (PFAD) molar ratio 15 :1, temp 65 °C, 2h, 16% AFS-CS,	-100% for LA -72.6% for (PFAD)	18
Oleic acid	1-methylimidazolium hydrogen sulfate, $[HMIM]HSO_4$, ionic liquid	8 h, 110 ± 2 °C, 15 :1 M ratio methanol/oleic acid and a catalyst dosage of 15 wt.%. 8 h, 110 ± 2 °C, 14 :1 M ratio and a catalyst dosage of 14 wt. %.	95 % 90%	60
Oleic acid	Zinc acetate	Molar ratio of methanol to oleic acid 4:1, 1 .0 wt.% zinc acetate catalyst, under pressure 6.0 MPa & 220 °C.	95%	61
Myristic acid	Sulfated zirconia (SZ) solid acid catalyst	Myristic acid to methanol molar ratio of 1:10, 0.5 wt.% solid catalyst, at 60 ^{o}C after 5 h.	98%, after five cycles reduced to 87%	62

Palmitic acid	H-Y and ZSM-5 zeolites as solid acid catalysts	Methanol to palmitic acid molar ratio 2 :1, 3 µmol of catalyst, at 70°C, reaction time 3h.	100%, promising recyclability	63
Oleic acid	10% and 20% WO3/USY/US zeolites	Methyl acetate to oleic acid molar ratio 10 :1, 10%, 20% cat., 240°C,	79.4 wt% and 80.8 wt%	64
Lauric acid	Ag_1 $(NH_4)_2PW_{12}O_{40}$/UIO-66	Lauric acid to methanol molar ratio 1:15, 10 wt. % catalyst, 150 °C for 3 h	75%, reduced to 58% on sixth recycle	65
Stearic, oleic, and palmitic acids	Montmorillonite-based clay catalysts (KSF, KSF/0, KP10, and K10)	2 g of FFA, in the presence of 0.2 g of montmorillonite KSF/0 (Cc = 0.1w/w) at 150 °C during 4 h using different alcohols. To have the same flow of alcohol (2×10^{-2} mol. Min^{-1}) and therefore a constant molar ratio acid/alcohol, the reactor was charged with different alcohol volumes : 195, 280, 360, 445 and 445 mL for methanol, ethanol, propanol, 1-butanol and 2-butanol, respectively.	97% 84% after three cycles).	66
Lauric acid	Niobic acid, niobium phosphate	Fatty acid (50 mmol), alcohol (500 mmol), 10wt. % catalyst, 120-160°C, 7h.	97%, no loss of activity after 3 cycles	67

5. Esterification reaction parameters

Esters are among the highest volume of industrial organic compounds produced. They are frequently employed in various domestic and industrial processes. Fischer esterification regarded as the most common and widely practiced process of ester synthesis, faces serious limitations of low conversion and high reaction time attributed largely to establishment of equilibrium. Ester hydrolysis, reverse reaction to esterification, starts by supply of a byproduct- water. Several approaches have been developed to avoid equilibrium establishment and to improve overall conversion and rate of reaction, a significant difference exists between the current industrial practices and optimum esterification process/conditions. In the following section, there are the discussion of some of those of reaction parameters should be optmized to make the reaction forward and increase the ester product.

5.1 Effect of molar ratio of FFA to alcohol

Many studies have been carried out on esterification reactions of long chain fatty acids with alcohol. As the esterification reaction is an equilibrium-limited reaction, an excess amount of methanol shifts the reaction equilibrium toward the right. Yet other authors have used excess alcohol to optimize their yield of ester over their catalyst. For example, molar ratio of lauric acid to methanol varied from 1 :3 to 1 :18 has been reported by Zhang Q. et al.[65], the rapid conversion of lauric acid from 46.2 to 75.6% was observed as the molar ratio of acid to methanol increased from 1 :3 up to 1 :15. However, they reported that further increase of the molar ratio led to a slight decrease in the conversion of the lauric acid. Excess methanol was thought to cause dilution of both the lauric acid and catalyst, resulting in reduced product [65]. This phenomenon has been seen in a number of other studies as for example in Ezebor F. et. al., where new catalysts prepared from oil palm trunk (OPT) and sugarcane bagasse (SCB) were used in the synthesis of ethyl palmitate and butyl palmitate. The optimum level of methanol to acid ratio was 18 :1, with further increases in methanol failing to lead to enhancement of catalytic performance, as too large excess could cause dilution of reaction system or even shield palmitic acid molecules from the catalyst active sites [68]. Similar observation was reported by other investigators [69,70,71], where FAME yield increases with increase in methanol/oil molar ratio, but too large excess had no positive effect.

Free fatty acids (FFA) were esterified with anhydrous methanol, using a methanol/oleic acid molar ratio of 20 :1– 80 :1 and 10 :1–114 :1 with a sulphuric acid catalyst concentration of 5% and 10%, respectively. Based on the experimental results, a methanol/oleic acid mole ratio of 60 :1, a catalyst (sulphuric acid) concentration of 5 wt. % and a temperature of 60 ˚C provided a final acid value for the oil lower than 1 mg KOH/g oil within 120 min [72]. Also, the effect of molar ratio of alcohol to acid from 4 :1 up to 8 :1 on stearic acid conversion has been investigated by Liu W. et al., molar ratio of alcohol to acid of 4 :1 provided the best conversion. They explained that a drastic drop of conversion with increased molar ratio of alcohol to acid from 4 :1 to 8 :1 can be attributed to the saturation of the catalytic surface with the alcohol or prevention of nucleophilic attack by shielding protonated alcohol by its own excess [59].

5.2 Effect of concentration and type of catalyst

It has been shown that by increasing the amount of catalyst, the number of acid sites also increases in the esterification of FFAs, which allows accessibility of a greater number of reactant molecules resulting in an increased yield of the ester. The effect of the amount of catalyst in the range of 1-12 wt. % on lauric acid conversion has been investigated by Zhang Q. et al. [65]. A novel solid acid nano-catalyst (Ag_1 $(NH_4)_2PW_{12}O_{40}$/UiO-66) comprising ammonium and silver co-doped $H_3PW_{12}O_{40}$ and zirconium-based metal–organic framework (UiO-66) was used in the conversion of lauric acid. The optimum amount of catalyst was 10 wt. %, and the rate of reaction was slightly increased with further increase of catalyst amount [65]. The effect of catalyst loading from 0.01–0.2% w/w over commercial acid clays (KSF, KSF/0, KP10, and K10) for conversion of stearic acid with ethanol, at 150 °C, for 4 hours has been studied [66]. Ester conversion increased proportionally with the concentration of catalyst ; whereas it was found to be independent of the catalyst concentration above 0.1 %w/w (97% of fatty acid was converted). The results obtained suggest that the initial activity increased with the total number of available active catalytic sites.

The esterification reaction of stearic acid with methanol and ethanol over cation exchanged montmorillonite K10 (MMT K10) was studied [58]. A series of Fe- MMT clay catalysts were prepared by adding 10 g of MMT K10 to 0.25, 0.5, 0.75, 1 M aqueous solution of Fe $(NO_3)_3$ at 80 ^oC for 8 h. These iron exchanged MMT K10 (Fe-MMT K10) clays were used to esterify stearic acid. The increase in ion concentration affected the percentage of conversion maximising at 0.75 M Fe-MMT K10, and then slightly decreasing for 1M Fe-MMT K10. High stearic acid conversion of 75% was obtained for 0.75 M iron concentration [58].

5.3 Effect of reaction temperature and alcohol types

The effect of reaction temperature was studied on esterification reaction of long chain fatty acids. As most of these long chain fatty acids are insoluble in methanol at room temperature, their solubility increases with temperature resulting in higher conversion as the higher temperature facilitates the protonation of the carbonyl group of the acid and favours the nucleophile attack of methanol on the acid. Many authors investigated the effect of temperature on FFA conversion such as ; a high temperature range from 110 to 160 °C performed on the esterification of lauric acid by Zhang Q et. al., [65]. It was found that there was a gradual increase in the lauric acid conversion on increasing temperature from 110 to 150 °C. However, a slight decrease in lauric acid conversion was observed beyond 150 °C, probably because there was a loss of methanol due to evaporation [65]. Other work on stearic acid showed increased conversion with increased temperature from 90 to 100 °C arising from an increased mass transfer rate. Higher temperatures are known to greatly accelerate reaction rate and improve the mass transfer limitation between reactant and catalyst. However, increase in temperature from 100 to 110 °C reduced stearic acid conversion, whilst conversion slightly changes with further temperature increase from 110 to 140 °C [59]. Their optimum reaction temperature was 100 °C, in order to save the energy of the process, as they didn't notice significant product conversion beyond 100 °C. In contrast, Bassan I. A.L. et. al. [67], found a maximum conversion of 80% for lauric acid esterification with methanol after 2 hr at the higher temperature of 160 °C in batch reactor [67]. The conversion of oleic acid over Amazon flint kaolin (MF9S4) solid acid catalyst increased with increasing temperature from 13.5% at 100 °C to 98.9% at 160 °C [59].

The effect of the different alcohols was evaluated in the esterification of fatty acids catalysed by different type of catalysts. The esterification of lauric acid with the alcohols methanol, ethanol, butanol using niobic acid with niobium phosphate catalyst was studied by Bassan. Reaction conditions were molar ratio alcohol : acid 10 :1, reaction time of 4 hours, catalyst concentration of 10% w/w in relation to fatty acid. For all the alcohols the reaction temperature was selected below the boiling temperature of each alcohol studied. The conversion of lauric acid was less than 35% with methanol and ethanol under atmospheric pressure. The highest lauric acid conversion results were achieved (around 81%) in the reaction with 1-butanol [67]. The esterification of acetic acid with ethanol, butanol and iso-pentanol catalysed by $Nb_2O_5/SiO_2–Al_2O_3$ where it was found that reactivity increased from ethanol to iso-pentanol [73].

In addition, Neji et al., evaluated different alcohols i.e., methanol, ethanol, propanol and butanol in the esterification of stearic acid catalysed by montmorillonite KSF/0 at 150 °C for 4 hours using semi-continuous reactor working above the boiling point of water and alcohol. This enabled continuous removal of the water produced which caused a shift in equilibrium towards esterification. In their study butanol which has the higher boiling point of 117.5 °C which evaporated at lower rate than the other alcohols at the reaction temperature of 150 °C, hence it gave the higher conversion of 99 % [66].

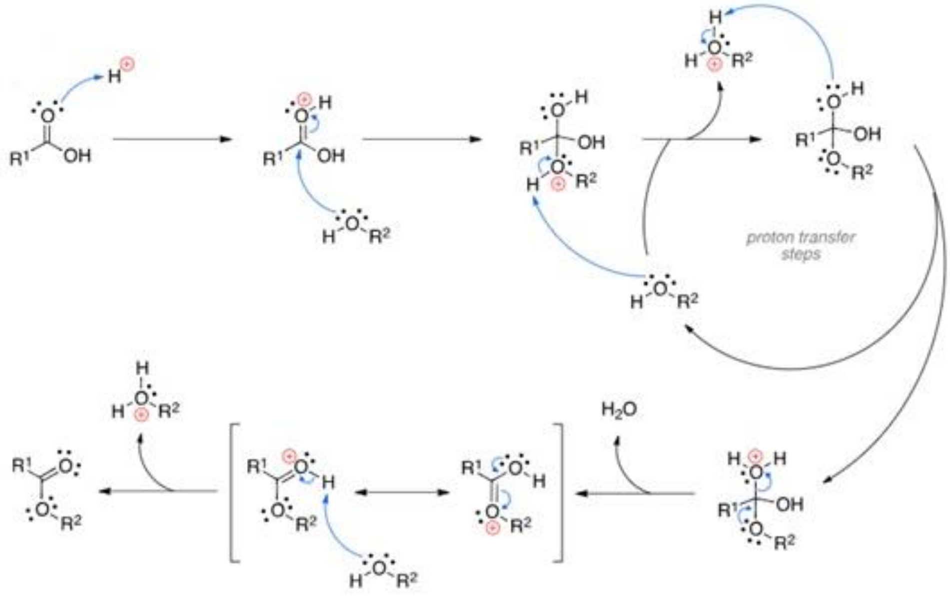
5.3 Effect of reaction time

Reaction time studies are useful in identifying product formation and reactant disappearance, as reported by Liu W. et al., in the esterification of stearic acid. Their results indicate that the esterification reached equilibrium after 4 hours, after which conversion decreases with further increase of reaction time to 7 hours [59]. However, the effect of reaction time in the esterification of lauric acid with 1-butanol has been reported over niobium phosphate catalyst by Bassan I. A.L. et al., in contrast their conversion was higher than 95% after 7 h [67]. In summary, all esterification reaction parameters are co-related to each other. For instance, the reaction time depends on reaction parameters, such as the acidity and amount/type of the catalyst, temperature, the molar ratio of acid to alcohol. For example, if the catalyst amount increases, it means more acid sites are available, and if the reaction temperature is high, the time to reach the equilibrium state is much shorter.

Further examples, the effect of reaction time for the esterification of stearic acid with ethanol and methanol has also been investigated by using iron exchanged Montmorillonite K10 Clay Catalysts. The conversion of stearic acid generally increased with increasing reaction time. In the initial 5 minutes of reaction, the conversion of the steric acid with ethanol was 47 % after which the reaction proceeded rapidly within 40 minutes to achieve a conversion of 65%. Then, the conversion remained almost constant until 180 minutes when it was only slightly increased to 68 %. Using methanol as the alcohol in the conversion of stearic acid to methyl stearate, the conversion exhibited a different reaction profile where in the first 5 minutes conversion of 68 % was achieved which increased over 180 minutes to 78 % [58]. The rate of esterification of oleic acid reached 98.9% on extending reaction time from 30 min up to 240 min using reaction conditions of acid : alcohol molar ratio of 1 :60 at 160◦C, over amazon flint kaolin (MF9S4) solid acid catalyst [74].

6.Mechanism of esterification reaction

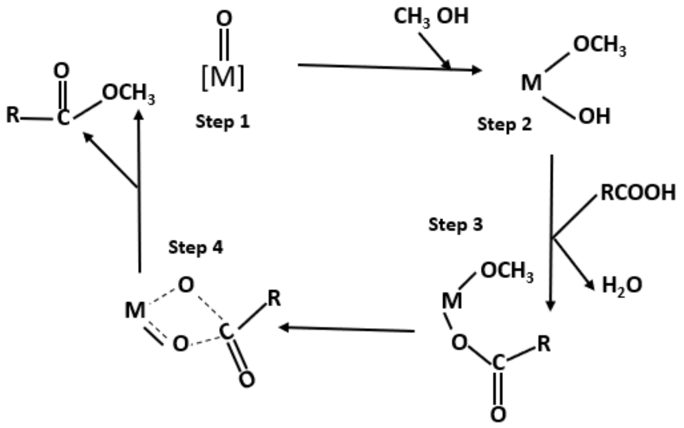
To an organic chemist, the term ester normally means an ester of a carboxylic acid. Replacing the group of a carboxylic acid with the group of an alcohol gives a carboxylic ester (See Fig. 1 Above). The general mechanism of carboxylic acid with alcohol in the presence strong acid such as sulphuric acid involved in five steps include: protnation of carboxylic acid, addition of alcohol, proton transfer, elimenation of water molecule and deportonation of hydrogen ion (See Scheme 1) [75]. Carboxylic acids can be esterified by alcohols in the presence of a suitable acidic catalyst as illustrated in Scheme 1. The initial step is protonation of the acid to give an oxonium ion, which can undergo an exchange reaction with an alcohol to give the intermediate, and this in turn can lose a proton to become an ester. Each step in the process is reversible but in the presence of a large excess of the alcohol, the equilibrium point of the reaction is displaced so that esterification proceeds virtually to completion. However, in the presence of water, which is a stronger electron donor than are aliphatic alcohols, formation of the intermediate is not favoured and esterification will not proceed fully [76].



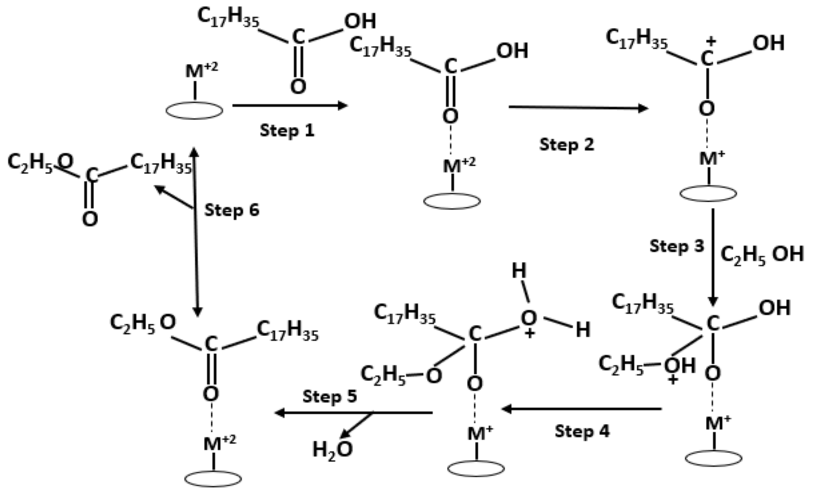
Scheme 1: Esterfication reaction mechanism of carboxylic acid with alcohol.

The mechanisim of esterification reaction has been proposed over heterogenous acidic catalyst by several reseachers. The feasible procedure for recovery and reuse besides the high yields of biodiesel suggest that the heterogenous acid catalyst are potentially useful for biodiesel production. Those authors proposed a mechanism of the soild catalytic action as described in Scheme 2, 3 & 4 [77,78,79,80,81]. The authors suggested that the molecules of fatty acid adsorbed on the surface of catalyst, due to interaction between metal cation present in the catalyst oxide (Lewis acid, M^{2+}) and electrons of the carbonyl group oxygen atom (base). So, the density of positive charge of carbonyl carbon increase due to this interaction and the nucleophilic attack takes place by electrons pair of the alcohol hydroxyl group. The resulting intermediate eliminates a water molecule and the ester formed. Finally, the surface of catalyst is free to participate in the next catalytic cycles [77-81].

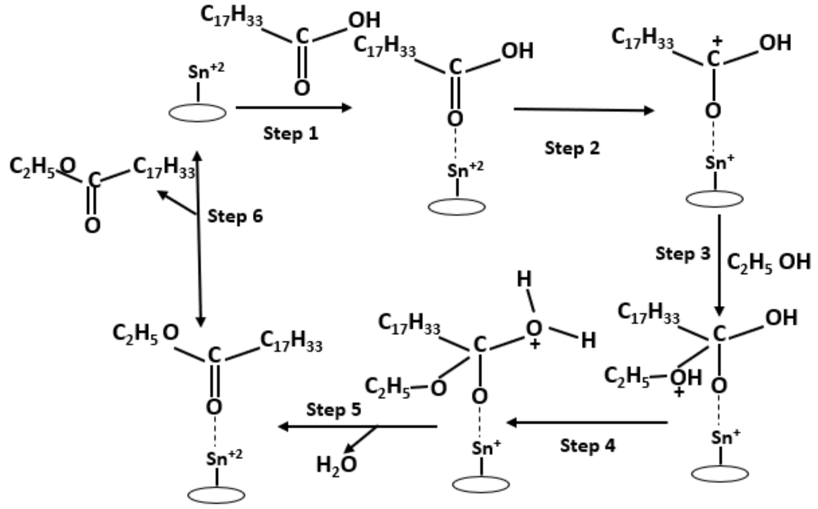
The mechanisms of the acid catalysed esterification involving heterogeneous catalysts is given by the general mechanism of scheme 2. Schemes 3 and 4 have also been added to show that two different solid acid catalysts using two different fatty acids follow the same general mechanism of scheme 2, whilst showing two more steps describing two additional mechanistic steps.



Scheme 2: Proposed mechanism for the esterification of fatty acids catalyzed by Lewis acid metal oxides [77, 78].



Scheme 3: Proposed mechanism for the esterification of stearic acid catalyzed by Lewis acid metal oxides (ZrO_2 supports on Al_2O_3, Fe_2O_3, TiO_2 and SiO_2) [79].



Scheme 4 : Proposal of a mechanism for the ester formation catalyzed by $SnCl_2/M_xO_y$ (M = Zr or Nb ; x=1 or 2 ; y=2 or 5) in the oleic acid esterification into ethyl oleate [80, 81].

In summary, the mechansim of heterogenous catalysis takes place over the surface of the metal supported catalyst, via several steps such as : Diffusion of the reactants through a boundary layer surrounding the catalyst particle ; intraparticle diffusion of the reactants into the catalyst pores to the active sites ; adsorption of the reactants onto active sites, surface reactions involving formation or conversion of various adsorbed intermediates, possibly including surface diffusion steps ; desorption of products from catalyst sites ; Intraparticle diffusion of the products through the catalyst pores ; diffusion of the products across the boundary layer surrounding the catalyst particle [82]. In contrast, the mechanism of homogeneous catalysis occurs in the following steps : protonation of the carbonyl oxygen, addition of the alcohol, proton transfer, elimination and deprotonation.

7. Challenges and Sustainability

The sustainability for developing the proposed FOG waste- biodiesel production has three main pillars : the environment, economy, and society. For the environmental aspects, the use of a low cost feedstock such as FOGs in wastewater effluent makes use of a waste commodity. The optimization of reaction parameters in particular reduced temperature and use of organic solvents (although these can be reclaimed) can achieve the conversion of FOG up to at least 94%. From economic aspects, FOGs are a potentially sustainable biodiesel feedstock due to their high FFA content, which on esterification not only produces biodiesel but also profitable side products of glycerol and K_2HPO_4 in an enviromentally eco-friendly stystem [21].

There is potential of using and recycling a low cost feedstock such as FOGs which causes severe environmental pollution, and blockage of sewers in developed countries such as the UK and USA. Also, fatty acid methyl esters (FAMEs) /biodiesel the outcome of esterification is a renewable energy with low carbon dioxide emission, zero or lower sulphur content and lower particulate matter emission especially of concern in the transportation sector. Nowadays, the global use of biodiesel as fuel is approximated at 10% and the aim is to increase this as a cleaner alternative energy for fossil fuel and traditional petroleum energy particlualy in transportation sector by 2050. To ensure social sustainability, a new framework of FOG-management could effectively cope with the related environmental problems and reduce the human environmental impact.

A challenge to the use of FOG_S as source for biodiesel production is that the composition of FOGs varies substantially among different sources which leads to inconsistency in FOGs characteristics causing variations in biodiesel characteristics, the production cost, and the optimum operation conditions. Another challenge is that it is difficult to develop an effecient heterogenous catalytic system to tranform feedstock based -FOGs to biodiesel production.

Heterogeneous catalysts can avoid the use of corrosive liquid acids and bases with associated storage and handling problems.

On the one hand, biodiesel production of FOGs is more difficultas it requires more steps than when processing pure oils, e.g. Purification of FOGs (filtration, purfication and water removal) and also requires an esterification step of the free fatty acids before the transesterification reaction which produces the biodiesel. On the other hand, it is very desirable to transform FOGs into fuel rather than using fresh oils, that could be otherwise be used in the food industry. If heterogenous acid catalysts could be as efficient in the esterification of FOGs as it is with fresh oil such as vegetable oil, this would motivate its use in industry, even if catalyst production increases some costs but, at the same time, decreases the associated costs of catalyst separation and purification after the reaction and indeed canenable catalyst re-use. Future steps should include an analysis of heterogenous catalyst usage in the transformation of FOGs into a biofuel.

9.Conclusion

This review has shown that the esterification of high free fatty acid lipid feedstocks from wastewater containing FOGs is an alternative route to biodiesel production as a renewable energy is possible. Based on this literature review, numerous studies have been done on the esterification of free fatty acids and their transformation into fatty acid methyl esters (FAMEs) which is the main constituent of biodiesel. The yield of biodiesel depends on a number of parameters ; such as catalyst concentration, catalyst type, and molar ratio of reactants, reaction temperature, and reaction time and optimization of these reaction conditions.

There are four primary factors affecting the yield of biodiesel, i.e. alcohol quantity, reaction time, reaction temperature, and catalyst concentration. To ensure a high yield of FAMEs, the molar ratio of alcohol to fatty acid should be increased to between 6 :1 up to 20 :1 with the use of an acidic catalyst. For used cooking oils or for oils with a high percentage of free fatty acids, a higher molar ratio is needed for the acid-catalysed reaction. Whilst the conversion rate of fatty acid esters increases with reaction time the yield of the biodiesel product reaches a maximum at an optimal reaction time. Higher reaction temperature can decrease the viscosity of oils, enhancing the reaction rate. The optimal temperature ranged between 90 °C and 160 °C for heterogeneous catalyst and in the range of 60 °C to 65 °C for homogenous acidic catalyst, depending on the amount of free fatty acids that the oil contains. The optimal condition of catalyst concentration is about 6 wt. % up to 10wt. % for heterogeneous solid acidic catalysts and between 3 to 5 %v/v for H_2SO_4 which is the most commonly used catalyst. Therefore, all reaction parameters are co-related to each other and all of them have significant influence on the reaction, therefore all parameters have to be optimized.

With increasing concern over global warming, it is foreseeable that biodiesel usage would continue to grow at a fast pace. This will trigger the development of more sophisticated methods of biodiesel production and refining to cope with the increasing market demand.

Acknowledgement

This work is supported by funding from the co-sponsors Daphne Jackson Trust, Society of Chemists in Industry (SCI) and Royal Society of Chemistry (RSC), and hosted at De Montfort University, Leicester. I also thank for Dr Pang for his revision.

10.Reference

[1] Bora A. P., Gupta D. P. and Durbha K. S., Fuel, 259 (2020), 116262.

[2] Tarigan J. Br., Ginting M., Mubarokah S.N., Sebayang F., Karo-karo J., Nguyen T. T.,Ginting J. and Sitepu E. K., , RSC Adv. , 9 (2019), 35109.

[3] Kouzu M., HIdaba J.S., *Fuel, 93(*2012), 1-12.

[4] Semwal, S., Arora, A.K., Badoni, R.P. & Tuli, D.K.,Bioresour. Technol.*, 102* (2011), , 2151-2161.

[5] Srivastava N., Srivastava M., Gupta V. K., Manikanta A., Mishra K., Singh S., Singh S., Ramteke P. W. And Mishra P. K., 3Biotech, 8 (2018), ,245.

[6] Dimian, A. C. and Kiss, A. A. J., Clean. Prod., 239 (2019), 2-42.

[7] Bashira M.J.K., Wong L. P., Hilaire D. St., Kim J., Salako O., Jean M. J., Adeyemi R., James S. , Foster T., Pratt L.M, J. Environ. Chem. Eng., *8*(4), (2020), 103848.

[8] Abomohra Abd El-F., Elsayed M., Esakkimuthud S., El-Sheekh M., Hanelt D., Prog. Energy Combust. Sci., 81(2020), 100868.

[9] Marchetti J.M. and Errazu A.F., *Biomass Bioenergy*, *32* (2008), , 892-895.

[10] Tran N., Tisma M., Budzaki S., Hessel V., Ind. Eng. Chem Res., 60(5), (2021),

[11] Cankci M., Bioresour. Technol., 98 (2007), 183-90.

[12] Montefrio MJ., Xinwen T., Obbard JP., Appl. Energy, 87 (2010), ,3155-61.

[13] Suto P., Gray D., Larsen E. Hake J., Proc. Water Environ. Fed., 2006 (2008), ,858-79.

[14] Parry DL, Vandenburgh S, Salerno M., 2008 (2008), 1045-62.

[15] Yousfi M., Bombarda I., Hamia C., Djeridane A., Stocker P., Gaydou E., Mediterr J Nutr Metab 2(2009) ,197–203.

[16] Sankaran R., Show P. L., and Chang J.-S., *Biofuels Bioprod. &Biorefin., 10,(*2016), 896–916.

[17] Daud N. M., Sheikh Abdullah S. R., Abu Hasan H. and Yaakob Z., *Process Saf. and Environ. Prot., 94,(2015),* , 487-508.

[18] Ganesan S., Nadarajah S. , Chee X. Y. , Khairuddean M. , Teh G. B., *Renewable Energy, 153(*2020), , 1406-1417.

[19]Mahmoud H. R. , El-Molla S. A., Ibrahim M. M., Renewable Energy, 160 (2020), , 42-51.

[20] Lee J., Jung J-M., Park C., Jeon B-H., Wang C-H., Lee S-R., and Kwon E. E., J. Cleaner Prod., 168,(2017), 1211-1216.

[21] Taipabu M. I., Viswanathan K., Wu W., Nagy Z. K., Chem. Eng. J. 424 (2021) 130199

[22] Ibrahim M. M., Mahmoud H. R., El-Molla S. A., Catal. Commun.,122(2019), , 10–15.

[23] Alismaeel Z .T., Abbas A. S., Albayati T. M., Doyle A. M. , *Fuel, 234 (2018)*, 170-176.

[24] Leyva F., Orjuela A., Miller D. J., Gil I., Vargas J. and Rodríguez G., Ind. Eng. Chem. Res., 52, (2013), 18153−18161.

[25] Banchero M. and Gozzelino G., Energies, 11 (2018),1843.

[26] Ilgen O., Fuel Process. Technol., 124, (2014), 134–139.

[27] Alhassani M. H., Al-Jubouri S. M., Noori W. O., Al-Jendeel H. A., International Journal of Engineering (IJE), IJE TRANSACTIONS B : Applications ,31(8), (2018), 1172-1179.

[28] Naik B. D., and Udayakumar M., Mater. Today : Proc., 46 (2021), 9855–9861

[29] Saravanan K., Tyagi B., Shukla R. S., Bajaj H C., Fuel, 165, (2016), 298–305.

[30] Saravanana K., Tyagi B., Shuklaa R.S., Bajaj H.C., Appl. Catal. B : Environ., 172–173, (2015), 108–115.

[31] Thushari I and Babel S. (2018). Bioresou. Technol., 248 , 199-203.

[32] Babayigit E., Atik Alper D. and Erdincler A., Waste Biomass Vaporization,9(2018), 2471-2479.

[33] Olkiewicz M, Fortuny A, Stüber F, Fabregat A., Font J., Bengoa C., *Fuel, 141(2015)*, 250–257.

[34] Qi J, Zhu F, Wei X, Zhao L, Xiong Y, Wu X, Yan F. ,Waste Manage.,49(2016), 212–220.

[35] Olkiewicz M., A Fortuny., Stüber F., Fabregat A., Font J., Bengoaa C., Procedia Eng., 42,(2012), 634 – 643.

[36] Mondala A., Liang K., Toghiani H., Hernandez R., French T., Bioresou. Technol., 100 (2009), 1203–1210.

[37] Pastore C., Lopez A., Lotito V., and Mascolo G., *Chemosphere,92*(6)*,* (2013), 667-673.

[38] Tarigan J. Br., Ginting M., Mubarokah S.N., Sebayang F., Karo-karo J., Nguyen T. T.,Ginting J. and Sitepu E. K., RSC Adv., 9 (2019), 35109.

[39] Tran N. N., Ho P. Q., Hall T., McMurchie E. J., Ngothai Y., J. Multidiscip. Eng. Sci. Studi., 3(2017), 1853-1859.

[40] Farooq M., Ramli A. and, Subbarao D., J. Cleaner Prod., 59(2013), 131-140

[41] Liang X., Xiao H., Qi C., Fuel Process. Technol., 110(2013), 109-113.

[42] Fatah M. A., Mansour M. S. and Fouad Y.O., Int. J. Chem. Biochem. Sci.,9 (2016), 33-43.

[43] Istadi I., Prasetyo S. A. and Nugroho T. S. ,Procedia Environ.l Sci., 23(2015), 394 – 399

[44] Feyzi M. and Norouzi L., Renewable Energy,94(2016), 579–586.

[45] Hu S., Guan Y., Wang Y., Han H., Appl. Energy, 88(8), (2011), 2685–2690.

[46] Reddy A.N.R., Saleh A.A., Isalm M.S., Hamdan S. and Maleque M. A., Energy Fuels, 30(1) (2016),334–343.

[47] Prabu M., Manikandan M., Kandasamy P., Kalaivani P. R., Rajendiran N., and Raja T., ACS Omega,4 (2019), 3500−3507.

[48] Endalew A. K., Kiros Y. and Zanzi R., Energy, 36 (5) (2011), , 2693-2700.

[49] Baskar, G. & Soumiya, S., Renewable Energy, 98(C),(2016), 101-107.

[50] Widayat W., Darmawan T., Hadiyanto H. and Ar Rosyid R., J. Phys.: Conf. Ser., 877 (2017), 012018.

[51] Olkiewicz M., Caporgno M. P., Fortuny A., Stüber F., Fabregat A., Font J. and Bengoa C.,Fuel Process. Technol., 128 (2014) , 331–338.

[52] Wang Y., Sha F., Xiaojuan B., Jingchan Z. and Siqing X., Waste Manage., Part A 47 (2016), 91-97.

[53] Tu, Q., Wang J., Lu M., Brougham A. and Lu T., Waste Manage., 54(2016), 126-130.

[54] Boz N., Degirmenbasi N., and Kalyon D. M., Appl. Catal. B : Environ., 165 (2015) 723–730.

[55] Zhang H., Tiana F., Xu L., Peng R., Y Li Y., Deng J., Chem. Eng. J., 388 (2020) 124214.

[56] Petchsoongsakul N., Ngaosuwan K., Kiatkittipong W., Aiouache F., Assabumrungrat S., Energy Convers. Manage. 153 (2017) 493–503.

[57] Ozbay N., Nuray Oktar N., Tapan N. A., Fuel, 87 (2008) 1789–1798.

[58] Almadani E. A., Radzi S. M., Harun F. W., Int. J. Appl. Chem.,12(1), (2016), 62-67.

[59] Liu W., Yin P., Liu X., Zhang S., Qu R., J. Ind. Eng. Chem., 21 (2015), 893–899.

[60] Roman F. F., Ribeiro A. E., Queiroz A., Lenzia G. G., Chaves E. S., Brito P,. Fuel, 239 (2019), 1231–1239.

[61] Song C., Qi Y., Deng T., Hou X., Qin Z. , Renewable Energy,35 (2010), 625–628.

[62] Saravanana K., Tyagia B., Bajaja H. C., Indian J. Chem. Sect. A,53(7),(2014),799-805.

[63] Prinsen P., Luque R., González-Arellano C., Microporous and Mesoporous Mater., 262 (2018), 133–139.

[64] Ketzera F., Celante D., de Castilhos F., Microporous and Mesoporous Mater.,291 (2020), 109704.

[65] Zhang Q., Yang T., Lei D., Wang J. and Zhang Y. ,ACS Omega, 5 (22), (2020), 12760–12767.

[66] Neji S. B., Trabelsi M. and Frikha M. H., Energies,2 (2009),1108-1117.

[67] Bassan I. A.L., Nascimento D. R., San Gil R. A.S., Pais da Silva M. I.,Moreira C. R., Gonzalez W. A., Faro Jr A. C., Onfroy T., Lachter E. R., Fuel Process. Technol., 106 (2013), 619-624.

[68] Ezebor F., Khairuddean M., Abdullah A. Z., Boey P. L., Energy ,70(2014), 493-503.

[69] Satyanarayana M, Muraleedharan C. A, Energy 36(4), (2012), 2129-37.

[70] Uzun BB, Kılıç M, Özbay N, Pütün AE, Pütün E. Energy ,44(1), (2012),347-51.

[71] Rasimoglu N, Temur H., Energy, 68(0), (2014), 57-60.

[72] Berrios M., Siles J., Martı´n M.A., Martı´n A., Fuel,86 (2007), 2383–2388.

[73] Braga V.S., Barros I.C.L., Garcia F.A.C., Dias S.C.L., Dias J.A., Catal. Today, 133-135 (2008), 106–112.

[74] Nascimento L. A. S., Tioto L. M. Z., Angelica R. S., da Costa C. E. F., Zamian J. R. and da Rocha Fiilho G. N. Appl. Catal. B-Environ., 101 (2011), 495–503.

[75] Wade JR. L. G., Organic chemistry, Ch. 21 : Carboxlyic acid derivatives, 8th Ed. (2013), USA, 981-1004.

[76] Christie W.W., in Advances in Lipid Methodology – Two, (1993), 69-111, [Ed. W.W. Christie, Oily Press, Dundee].

[77] Silva M.J. D., Cardoso A.L, J. Catal. 2013 (2013) 1–11

[78] Mello V. M., Pousa G. P. A. G., Pereira M. S. C., Dias I. M., and SuarezP. A. Z. Fuel Process. Technol., 92 (1), (2011), 53–57.

[79] Ibrahim M. M., Mahmoud H. R., El-Molla S. A., Catal. Commun. 122 (2019) 10–15.

[80] Cordeiro C. S., Silva F. R. D., Wypych F., and Ramos L. P., “Heterogeneous catalysts for biodiesel production,” Quimica Nova, 34 (3), (2011), 477–486.

[81] Yan S., Salley S. O., and Ng K. Y. S., Appl. Catal. A, General, 353 (2), (2009), 203–212.

[82] Ertl G., Knozinger H., Schuth F., Weitkamp J., Handbook of heterogenous catalysis, 2nd Ed., Vol 1., Ch. 1, P.2, Wiley-VCH.

Bibliography

Dr. Rawaz Ahmed : She received a scholarship from Kurdistan to pursue a Ph. D in heterogeneous catalysis on the dry reforming of methane at bteeside University, UK, which was followed by a 1 year Post Doctoral Fellowship in the hydrothermal conversion of poultry litter for nutrient recovery also at Teesside University. She won first prize for her poster at the Royal Society of Chemistry Conference in March 2011, and this work resulted in a patent application (P136962GB). She then spent 5 years as a lecturer at Kurdistan Institute for Strategic Study and Scientific Research (KISSR). Since October 2021 she is a Daphne Jackson Fellow funded by both the Royal Society of Chemistry and Society of Chemists in Industry (UK) hosted by Professor Katherine Huddersman at De Montfort University, Leicester, UK. Here she is focussing on the application of a heterogeneous catalyst in the esterification/tranesterification of FOGs from wastewater for the production of biodiesel.

Professor Katherine Huddersman is a Professor of Environmental Chemistry at De Montfort University focussed since 1996 on the production, characterisation and applications of a heterogenous modified polyacrylonitrile catalyst which is surface functionalised to enable iron complexation. She has applied this oxidation catalyst to wastewater treatment, disinfection and the production of chemicals. She is the recipient of over £4M of funding from UK governmen.

Review of biodiesel production by the esterification of wastewater containing Fats Oils and grease (FOGs)

Rawaz Ahmed and Katherine Huddersman

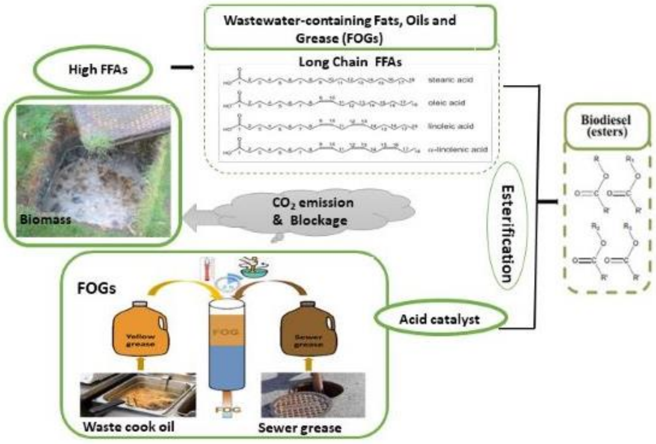
Faculty of health and life science at De Montfort University/Leicester

Email: huddzeo1@dmu.ac.uk and rawaz.ahmed2@dmu.ac.uk

Abstract

A promising solution for the near future is the substitution of non-renewable fossil fuels with a sustainable liquid feedstock for biofuel (biodiesel) production. The cost of conventional biodiesel production is higher than that of petroleum-based diesel production since it is produced mostly from expensive high-quality virgin oil. 70–80% of the overall biodiesel production cost is associated with the cost of raw materials. Brown grease (with free fatty acid levels > 15%) is created from rendered trap waste and is known as Fats, Oils, and Greases (FOGs). It is a potential source of biodiesel feedstocks and is available at no cost. Many researchers are interested in using low-cost high Free Fatty Acid (FFA) oils as the feedstock for biodiesel production.

This paper reviews the effect of feedstock pre-treatment and process parameters on the conversion of FOGs-wastewater to biodiesel by esterification, including alcohol to oil molar ratio, reaction temperature, reaction time, catalyst amount.



Sustainable biodiesel from Wastewater containing FOGs

Keywords: Fats Oils and Grease (FOGs); Esterification; Free fatty acid; methyl ester

Highlights

- Literature review on the esterification/transesterification catalytic processes in biodiesel production
- Highlighting the use of Fats, Oils, and Greases (FOGs) from wastewater.
- Reduction of high Free Fatty Acid (FFA) content of FOGs by esterification to methyl/ethyl ester
- Evaluation of the esterification reaction conditions, such as temperature, time, types of catalyst, and alcohol.

Contents

1. Introduction

Bio-fuels are gaining worldwide attention as an alternative fuel option replacing the usage of the mineral diesel derived from conventional fossil sources. The production of fuels from renewable biomass replacing the currently used traditional sources [1]. Among liquid renewable energy, biodiesel has been identified as able to be used directly in a diesel engine without requiring any modification [2]. Biodiesel is a fuel derived from edible and non-edible oils made by chemically reacting lipids such as animal fat (tallow), soybean oil, or some other vegetable oil with an alcohol producing a methyl, ethyl, or propyl ester [3, 4]. It is well known that the major cost involved in biodiesel production technology is dependent upon the used feedstock as virgin oil. The non-edible oil such as FOG is a lipid-rich waste in wastwater can be considered as a potential feedstock owing to its low cost and abundant availability [1,5,6]. Among the different renewable liquid feedstock's that have been studied, wastewater containing Fats, Oils, and Greases (FOGs) is the least explored one for biodiesel production. A recent analysis of brown grease (discharged into the sewer system) contained 60 % FOGs, 25 % water, and 15 % biosolids by mass [7]. Direct discharge of FOG clogs up the pipes and disturbs the plumbing of individual housing resulting in property flooding. The serious consequences of sewer pipes blocking results in sanitary sewer overflows (SSO) which further causes unhealthy environmental and hygiene deteriorations. Recently, the major causes of sewer blocks were attributed to FOG in many counties like US (50%), Malaysia (70%) and UK (50%), with an estimated annual cost of about US$ 25 billions for removal of this sewer blockage in US alone. Thus, FOG deposition is a precedent alarm globally which requires an effective management. Beyond a few measures, no sustainably effective managements have so far been devised. Hence, this issue needs to be adressed before it gets even bigger because of growing population and eventual urbanization [8].

One of the promising solutions to these problems is the challenges to developing eco-friendly, lower-environmental impact and more sustainable technology to convert FOGs found in wastewater into renewable energy (biodiesel). Thus, the coversion of FOGs to biodeisel production via transesterification/esterification reactions (See Fig.1 and Fig.2) also has been successfully investigated [9][10].

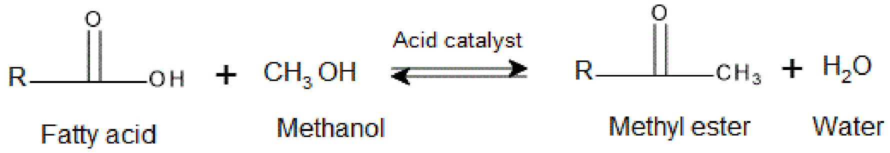


Figure 1 : Esterification reaction for biodiesel synthesis [9].

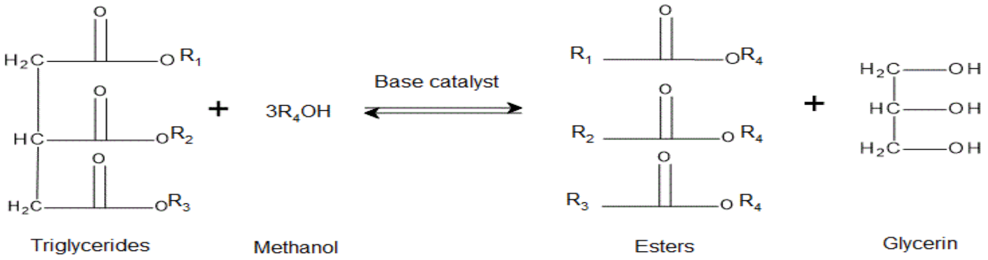


Figure 2 : Transesterification reaction for biodiesel synthesis [9].

Where R_1, R_2, R_3 and R_4 denotes any hydrocarbon chain. Since both reactions are equilibrium reactions, the molar relation of alcohol/oil should be over the stoichiometric amount to be able to achieve a good conversion of the FFA as well as of the triglyceride (TG).

Fats, oils and greases (FOGs) composition varies according to the country, region and different sources. For example, FOG obtained from restaurants contains about 15% FFAs, which entirely depends upon the source of FOG. Based on FFAs content, FOG can be classified into two main groups, namely yellow grease (less than 15% FFAs) and brown grease (above 15% FFAs) [11]. For instance, about 8% FFAs content was detected in grease interceptors located in the canteen of National University of Singapore [12]. Suto et al. [13] analyzed 27 different restaurant grease samples and recorded about 48% of saturated fats, whereas it was not determined in the dewatered restaurant grease anayzed by Parry et al. [14]. Analytical study of the fatty acid, triglyceride (TAG) and tocopherol composition of oil extract from the fruit of Algerian tree Argania spinosa found that the oil was found to contain trisaturated (0.47%), disaturated (9.3%), monosaturated (43.95%) and triunsaturated (45.20%) FA. The oil was characterised by a relatively high amount of tocopherols (1027.8 mg/kg). The (γ+β) -tocopherols were the major isomers, with the rest being α- and δ-tocopherols [15]. Thus, the profile and concentration of total fatty acids largely depend upon the sources generating FOG.

Table 1 shows the fatty acid profile of different FOG in comparison with other edible feedstocks.

Table 1 : Fatty acid profile of different types of fat, oil and grease (FOG) in comparison to the common edible feedstocks [8].

Fatty acids	Different kind of FOGs							Edible feedstocks			
	FOG		Yellow grease			Brown grease		Corn	Sunflower	Soybean	Rapeseed
Caprylic acid (C8 :0)	nd	0.9	nd	nd	nd	nd	nd	nd	nd	nd	nd
Capric acid (C10 :0)	nd	1.3	nd	nd	nd	nd	nd	nd	nd	nd	nd
Luric acid (C12 :0)	nd	3	nd	nd	nd	nd	nd	nd	nd	nd	nd
Myristic acid (C14 :0)	1.3	8.4	2.43	nd	1.4	1.7	1.66	0.2	0.1	nd	nd
Palmitic acid (C16 :0)	38.3	23.1	23.24	16	37.5	22.8	22.83	13	5.5	11.6	3.49
Palmitoleic acid (C16 :1)	1.2	nd	3.79	nd	3.1	3.1	3.13	nd	0.1	0.3	nd
Stearic acid (C18 :0)	7.2	9.8	12.96	5.21	4.8	12.5	12.54	2.5	4.7	4.2	0.85
Oleic acid (C18 :1)	36.9	36.1	44.32	34.28	36.3	42.4	42.36	30.5	19.5	21.6	64.4
Linoleic acid (C18 :2)	15.1	15.3	6.96	40.76	15.2	12.1	12.09	52.1	68.5	53.7	22.3
Linolenic acid (C18 :3)	nd	nd	0.67	nd	nd	0.8	0.82	1	0.1	7.5	8.23
Arachidic acid (C20 :0)	nd	2.1	nd	nd	nd	nd	nd	0.5	0.3	0.8	nd
Eicosenoic acid (C20 :1)	nd	nd	nd	nd	nd	nd	nd	0.2	0.1	0.3	nd
Benhenic aicd (C22 :0)	nd	nd	nd	nd	nd	nd	nd	nd	0.9	nd	nd
Others	0	0	5.62	3.75	1.7	4.6	4.57	0	0.2	0	0.73
Reference	12	13	11	14	12	11	11	15	15	15	14

nd : non detectable

Esterification is an industrially important process utilized for pharmaceutics, food, flavourings, and biofuels (biodiesel). Esterifying long chain free fatty acid (FFAs) using homogenous acid catalyst is a promising solution to take advantage of high free fatty acid content of FOGs from a wastewater feedstock to obtain a renewable energy i.e., biodiesel [9,16,17]. The traditional transesterification processes using homogeneous base catalysts such as KOH or NaOH are found to be not suitable for processing these types of feedstocks. This is due to the high free fatty acid (FFA) and moisture content in the FOGs wastewater will cause saponification during the transesterification reaction of Figure 2 and hence, lower the yield of esters. In order to overcome this situation, acid catalysts are used to lower the free fatty acid content by esterification before the transesterification process. Strong acid catalysts which are less susceptible to the influence of free fatty acid can simultaneously esterify and Trans-esterify low quality feedstock's simplifying the biodiesel production from low cost and high FFA content feedstock [18].

Biodiesel or alkyl esters of fatty acids are commonly produced using homogeneous acid catalysts such as H_2SO_4, HCl and H_3PO_4 in the esterification reaction. Homogeneous acid catalysed reactions can produce environmental and corrosion problems. In green technology, heterogeneous acid catalysts were shown to be the best alternative to homogeneous catalysts due to their easy separation of products, recovery and recyclability with less waste emission hence, reducing the environmental impact and process costs [19].

For example in the study of Lee and his colleagues, the conversion of fat, oil and grease (FOG) into fatty acid methyl esters (FAMEs) without pre-treatment of FOG was investigated. A thermally induced process to accomplish simultaneous esterification of free fatty acids (FFAs) and transesterification of lipids was introduced. Despite high contents of impurities in FOG (~14 wt. %), the maximum achievable yield of biodiesel/FAMEs (fatty acid methyl ester) on feedstock mass basis was >86% for 10 s reaction time without removal of impurities prior to the reaction while conventional acid catalysed reaction only produced less than 27.7 % of biodiesel from FOG [20]. Also the most current pablication, Taipabu et al. [21] has fouced on Production of renewable fuels and chemicals from fats, oils, and grease (FOG) using homogeneous and heterogeneous catalysts based on computianla design via both esterification and transesterification reaction. The optimum operating conditions reported that of Est-Design-2 and TransEst-Design-2 are 100 ◦C of reaction temperature at 480 min, and the molar ratio of methanol to oleic acid with 9 :1, and 75 ◦C of reaction temperature at 63 min, and the molar ratio of methanol to triolein with 3.84:1, respectively [21].

In recent times, different heterogeneous catalysts were developed and used for the esterification reaction, optimisation of reaction parameters and these include ZrO_2/SiO_2 catalysts [19], ZrO_2 based solid acid heterogeneous catalysts [22] and zeolite catalysts [23], amberlyst 70 catalyst [24], Amberlyst-15 resin catalyst [25], Amberlyst 46 resin catalyst [26], Amberlyst- 15 ion exchange resin [27], sulfated montmorillonite clay acidic catalyst [28], Sulfated zirconia solid acid catalyst[29], template-assisted mesoporous sulfated zirconia solid acid catalyst [30].

This review focuses on hetrogenous catalysis in the pretreatment of esterification of high free fatty acid lipid feedstock from wastewater containing FOGs and their transformation to biodiesel as a promising solution to achieve renewable energy in near future. Esterification of FFA to alkyl esters in the presence of an acidic catalyst is a route to improving the use of high FFA oils (e.g. some animal and vegetable oils) in biodiesel production. This work aims to review and understand the parameters that affect the conversion of fatty acids reacted with short chain alcohols to achieve better biodiesel yields.

2. Literature review

An extensive literature review has been carried out in order to assess the advantages and disadvantages of the catalytic esterification/transesterification for recalcitrant FOGs wastewater (see Tables 2 and 3). A summary of work performed so far shows that catalyst structure, morphology, texture, optmization reaction parameters such as tepmerature, catalyst concentration, reaction time, alcohol to substrate molar ratio, type of alcohol have a significant influence on the catalytic activity of biodiesel production from wastewater. Despite a large number of studies carried out on the catalytic esterification of FFAs in FOGs wastewater, there are still a number of drawbacks that hinder industrial application. Therefore, there is a need to develop cheaper more efficient catalysts that are less energy demanding in terms of their process conditions and that have optimal lifetime stability.

Moreover, conventional cation ion-exchange resins, composed of sulfonic acid groups as the active site, can offer better selectivity towards the desired product(s) and better reusability compared with homogeneous acid catalysts. Cation ion-exchange resins have been widely used for esterification and transesterification reactions because they are non-corrosive and easy to be separated from the reaction mixture. The use of resin-supported strong solid acids have become established as replacements for traditional catalysts in the efficient overall production of biodiesel from biomass feedstocks with high free fatty acids (FFAs) content. Recent progress in this field has proved the technical viability as well as the sustainability of this approach. Sulfonic ionic exchangers are the most widely investigated members of the series, though an ever-increasing number of studies focuses on alternatives to traditional polymer based ion-exchange resins e.g. sulfonic micro- and mesoporous materials, acidic ionic liquids, ionomeric membranes, and organic-inorganic hybrids. Most of these resin-supported solid acids showed promising reactivity toward esterification of FFAs. In contrast, the (very limited) amount of data available with respect to their reactivity toward transesterification reactions, indicates that this is still unsatisfactory, especially for industrial applications.

Table 2 : Comparison of the performance of homogenous catalysts on waste oil feedstock for biodiesel production

Catalyst	Feedstocks	Transesterification/ esterification reaction conditions	Biodiesel yield	Cycles	Ref.
H_2SO_4, ferric sulfate co-catalyst ($Fe_2(SO_4)_3$)	Brown grease from wastewater plant	Response Surface Methodology (RSM) was used to evaluate the correlation between the process variable and the response. Optimized conditions were 35 ml MeOH, 1.3 ml H_2SO_4, and reaction time of 120 min.	99.70 %	30 runs	7
H_2SO_4	Fats, Oils, and Grease (FOGs) Without treatment	-Methanol to feedstock molar ratio of 30, and (H_2SO_4 to FOGs feedstock molar ratio of 1.3); - Thermal esterification/transesterification at 240 °C to 350 °C and 10 s reaction time., 10 mL of FOGs, 200 mL of methanol, and 100 mg of silica were used,	> 86%		20
Acid catalyst synthesised using coconut meal residue (CMR)- CMR-DS-SO_3H	Grease Trap wastewater (GTW)	Methanol : oil (molar ratio) (6 :1–16 :1), reaction time (6– 16 h), and (5 %wt.) catalyst loading at 65–70° C. CMR-DS-SO_3H catalyst had high acid density (3.8 mmol/g).	> 80%	4	31
Acidic homogeneous Catalyst HCl	Wastewater treatment plant (WWTP) municipal sludge	Novel direct liquid-liquid lipid extraction used as pre-treatment of feedstock. Compared to standard drying method, direct liquid-liquid lipid extraction resulted with 53% higher lipid and 56% higher biodiesel production.	56%		32
HCl	Wastewater treatment plant (WWTP) municipal sludge (Primary, secondary, blended and stabilised sludge)	The influence of pre-treatment methods (ultrasonic and mechanical disintegration) was tested, but it did not increase significantly the amount of extracted lipid as well as biodiesel yield.	19%	4	33
H_2SO_4	Two type of WWTP sewage sludge obtained from the anaerobic–anoxic–oxic (A^2 /O)	-Methanol-to sludge mass ratio of 10 :1, a temperature of 60 °C, and a H_2SO_4 concentration of 5% (v/v), (from A^2 /O reactor).	96.7%		34

	and membrane bioreactor (MBR) processes as lipid	- Methanol-to-sludge mass ratio of 8 :1, a temperature of 50 °C, and a H_2SO_4 concentration of 5% (v/v), (from MBRreactor)	92.7%		
H_2SO_4	Wastewater treatment plant (WWTP) municipal sludge (Primary, secondary, blended and stabilised sludge)	The lipid sample (up to 50 mg), dissolved in 1 mL of hexane. After that, 2 mL of 1% sulfuric acid in methanol was added, heated overnight at 50 ˚C. 5 mL of 5% sodium chloride in water was added and the FAMEs were extracted 2 times with 5 mL of hexane.	87%	2	35
H_2SO_4	WWTO-Municipal wastewater sludges primary and secondary	75 °C, 5% (v/v) H_2SO_4, and 12 :1 methanol to sludge mass ratio.	75%	/	36
H_2SO_4	- WWTP : dried sludge, - WWTP : dewatered primary sludge	-10 g of dried sludge were suspended in 100 mL methanol with 0.25 mL of H_2SO_4 (96%), kept at 65 °C for 7 h.- 150 g of dewatered primary sludge mixed with methanol (300 or 750 mL) and 1.5 mL of sulphuric acid (96%). Kept at 65 °C for 7 h.	60.7% 85%	4	37
A homogeneous base, KOH and acid, H_2SO_4 catalyst	Waste spent coffee grounds (SCG)	Combines simultaneous soxhlet extraction-esterification/transesterification in a single step to produce biodiesel directly from wet SCG, molar ratio of co-solvent methanol to hexane of 1 : 2 and reaction time 30 min, 10 g of wet SCG biomass, 0.75 M of KOH or H_2SO_4 was used as catalyst. Base catalyst showed superior catalytic activity	97%	5	38
H_2SO_4	Fats, oil, and grease (FOG), the main composition of dewatered grease trap waste (GTW)	After Hexane extraction of FOGs, the FOG – ethanol molar ratio was 1 :3, 3 wt. % H_2SO_4 based on the amount of FOG, the reaction temperature was set at 65°C and the stirring speed was kept at 300rpm	96 %		39

Table3 : Comparaison of the performance of heterogeneous catalysts in biodiesel production

Catalyst	Feedstocks	Method of synthesis	Transesterification/ esterification reaction conditions	Biodiesel yield %	Cycles	Ref.
Mo-Mn/γ-Al_2O_3 bimetallic catalyst containing 15 wt. % MgO	Waste cooking oil (WCO)	Bifunctional heterogeneous catalysts were prepared using a modified wet impregnation method	Methanol to oil molar ratio of 27 :1 and an agitation speed of 500 rpm, 100 °C, 4h.	91.4	8	40
Novel acidic ionic liquid polymer	Fried cooking oil	Copolymerization of acidic ionic liquid oligomers and divinylbenzene (DVB)	Methanol : rapeseed oil 16 :1 molar ratio, temp. 70 °C, 12 h, The optimal amount of the catalyst was 50 mg.	99.0	6	41
Saw dust (used as the heterogeneous nano catalyst)	Waste cooking oil	Chemical activated : dried saw dust is mixed with hot sulphuric acid and stirred until the slurry mixture solidified. - Physical activation : dried saw dust calcinated from 600 ˚C - 1000 ˚C	Esterification by using H_2SO_4. The best yield at : a methanol : oil =8 :1, catalyst (5w/w%), temp.50 ºC, 1.5 h at 600 rpm for chemical activation. The best yield at : a methanol : oil = 12 :1, catalyst (5%), temp. 60 ± 1 ºC, 1.5 h at 600 rpm for physical activation.	Physically activated 65.5, chemically activated ,90	NA	42
Solid base catalysts (K_2O/CaO-ZnO)	Soybean oil	Co-precipitation method and impregnation method	Temp.60 ^{0}C, catalyst loading of 2 wt. %, methanol to oil ratio =15 :1, time 4 h. The incorporation of K_2O on the CaO-ZnO catalyst enhanced the catalytic activity due to increased basicity and surface area.	81.08	NA	43
CaO/Fe_3 O_4 @SiO_2	Waste sunflower oil	Combination of sol-gel and incipient wetness impregnation methods	Catalyst 6 wt. % ; oil to methanol molar ratio 1 :15 ; Temp. 65°C ; mechanical stirring 500 rpm ; time 5 h.	97	Several batch	44

A nano-magnetic catalyst KF/CaO–Fe_3O_4	Stillingia oil	Facile impregnation method	Reaction is carried out at 65 °C with a methanol/oil molar ratio of 12 :1 and 4 wt. % catalyst, 3 h of reaction time.	95	14	45
CaO powder	Crude Jatropha oil	Calcination–hydration dehydration of Polymesoda erosa shells how does this relate to CaO	Catalyst ratio to oil : 0.02:1 (w/w%) ; reaction time 133.1 min ; oil/ methanol molar ratio 1 :5.15 ; temperature 65°C ; stirring rate 500 rpm	95.8	9	46
Novel Mg/Al/Zn Hydrotalcite/SBA-15	Soybean oil (SBO)	Sol-gel method one pot preparation	The pelletized (0.5–0.8 mm) 1 mL catalyst was sandwiched between glass wool and ceramic beads in an Inconel reactor, reaction temp. Range= (180–300 °C), reaction time of 2 h. oil to methanol ratio= (1 :5–1 :30).	90	> 200 h TOS	47
CaO, Li- CaO catalyst, $Fe_2(SO_4)_3$ solid acid, CaO +$Fe_2(SO_4)_3$ mix Li- CaO +$Fe_2(SO_4)_3$	-Jatropha curcas oil - rapeseed oil	CaO was prepared by decomposing pulverized $CaCO_3$ at 960 ˚C for 3½ h. Lithium doped calcium oxide (Li-CaO) was prepared by the incipient wetness or impregnation method.	Temp. 60 ° C, 3 h time, molar ratio of alcohol to oil = 6 :1, 5 wt. % catalyst (based on the amount of oil), 300 rpm. Single step transesterification /esterification performed over mixed acid-base catalyst (CaO : $Fe_2(SO_4)_3$ = 3 :1 & Li- CaO : $Fe_2(SO_4)_3$ = 3 :1).	93.3 CaO/$Fe_2(SO_4)_3$ 96 Li /CaO/ $Fe_2(SO_4)_3$	3	48
Iron (II) doped ZnO nano-catalyst	Castor oil	Impregnation method	50 min at 55 °C with 14 wt % catalyst loading and 12 :1 methanol/oil ratio.	91		49
CaO derived from, $CaCO_3$, -Ca $(OH)_2$, -limestone	Palm oil	Thermal processing in a muffle furnace at 900° C	Esterification : A 800 ml cooking oil was mixed with 10 ml H_2SO_4, methanol to FFA molar ratio 40 :1, heated to 60 °C, 600 rpm, time 2 h. Transesterification : 100 ml of cooking oil filled into ultrasonic reactor. Mole ratio methanol to oil 9 :1 and catalyst loading 2.6 wt. %, for 40 minute.	85.15% for Ca $(OH)_2$; and 78.71% for $CaCO_3$ catalyst.	NA	50

Amberlyst-15 (A-15) Amberlyst-35 (A-35) Amberlyst-16 (A-16) and Dowex HCR-W2	Free fatty acids (FFA) in waste cooking oil (WCO)	Amberlyst and Dowex HCR-W_2 resins, dried for 12 h after washing with methanol 110 °C and 105 °C	20 vol.% methanol with 10g of FFA, at 50- 60 °C with 1- 2 wt% catalyst, samples were taken at 3, 5, 10 min and every 20 min of reaction time.	A-15 > A-35 > A-16 >	NA	51
Amberlyst 70 ion exchange resin	FFA, propionic acid	Amberlyst 70 resin washed, dried at 80°C, for 24 h.	Acid to alcohol molar ratios ,1 :2, 1 :1, and 2 :1, 80 °C up to 120 °C, and catalyst loadings (8.0, 4.0, and 0.8 wt % , 150 min reaction time.	69-71%	NA	24
Amberlyst-15	FFA : lauric, myristic, palmitic and stearic acid	Sulfonated cation-exchange resin Amberlyst-15, in dry, hydrogen form.	Optimum acid to methanol molar ratio 1 :5, at 150 ◦C, 7 wt. % of cat. ,400 min reaction time.	86%	NA	25
Amberlyst 46	FFA : oleic acid	As recieved Amberlyst -46 used directly	Methanol to Acid molar ratio 3 :1, 100 °C, 15wt. % catalyst and 2 h reaction time.	96.8-98.3%	10	26
Amberlyst-15	FFA : Acetic aicd (AcOH)	Amberlyst-15, overnight dried at 100°C.	Acid to ethanol molar ratio was 1 : 4, at 70°C, 4mg of cat., at 90 min reaction time.	70%	NA	27
Amberlyst -45	Vegetable oil, methanol, ethanol	Catalyst washed, dried at 110°C, 24h	Oil/alcohol molar ratio 1 :18, with 10wt. % of catalyst at 170 °C, 360min reaction time.	77.2%	5cycle 70.2%	52
Amberlyst-15 (A-15) Amberlyst-35 (A-36) Amberlyst-IR120 (A-IR120)	Sludge lipid from wastewater	Resins dried at 105◦C, the resin was kept in contact with methanol at 50-60°C for 2h.	In situ transesterification with sewage sludge as raw material. Amberslyst IR120/Sludge molar ratio 1 :2, methanol/Sludge molar ratio 33 :1, at 120°C, 21h.	32.9% A-IR120	6 cycles	53

In summary, Tables 2 and 3 show two main types of acid catalysts used in the esterification of bio-oilsthat is, mineral adcids and soild acid catalysts. The difference between the two types of catalysts can be remarkable. Mineral acids such as H_2SO_4 and HCl have strong acidity and hydrogen ions disperse homogenously within the esterification reaction. The steric barrier for the long chain free fatty acid of bio-oil molecues to access the hydrogen ion is small. In addition, it is difficult to deactivate the mineral acid catalysts from promoting a polymerisation reaction in the liquid medium, as the H^+ ion is not confined on the surface of the support. In comparsion, solid acid catalysts like soild acidic resins (e.g., Amberyst-15, 70) show quite different physico-chemical properties. The hydrogen ions are confined in the local vicinity of the catalyst, but not dispersed homogeneously in the reaction medium. Filling of the pores of the catalyst via polymerization could easily deactivate the catalyst. Compared with mineral acids, the local concentration of hydrogen ions on or near the extranal and internal surface of a soild acid catalyst is much higher than that in the bulk reaction medium.

There are other advantages of soild acid catalyst, thus soild acid catalysts are less corrosive than mineral acids to the material of the reactor. They can be easily separated and recycled, while separation of mineral acids from the liquid products is very difficult, requiring further purifaction procesess which are costly and energy intensive. Therefore, soild acid catalysts have greater potential for the esterification of bio-oil, due to their recyclability and low corrosiveness. However, its important to understand how the dispersion of hydrogen ions and steric effects affect the esterfifation of bio-oil, so as to provide essential information for the develpoplement of an effective soild acid catalyst for bio-oil esterification.

3. Esterification-Transesterification reaction of FOGs

Biodiesel can be produced by three technologies:

1. Alkaline catalyzed transesterification (suitable for feedstock with low free fatty acid content).

2. Acid catalyzed transesterification/esterification (good for feedstock with high FFA content).

3. Tranesterification double step process (good for feedstock with high FFA content).

In general, alkaline metal hydroxides or methoxides are very effective catalysts for transesterification. The rate of alkaline catalyzed transesterification is about 4000 times faster than acid catalyzed transesterification, but its drawback is that FFA cannot be converted to ester. The FFAs are only neutralized to fatty soap, which further complicates the separation causing an additional loss of biodiesel in the separation step.

Acid is a good catalyst for both esterification and transesterification, however the rate of transesterification is very much slower thanthat of esterification. This is the reason why some researchers chose the double step process for high FFA feedstock (esterification of FFA with acid catalyst followed by alkaline catalyzed transesterification). Total reaction times are still shorter than those experienced in the one step acid catalysis.

Fat/vegetable oil is primarily a triglyceride (glycerol ester of fatty acids), whereas Biodiesel is the mono- methyl ester of fatty acids. For this reason, biodiesel production process is a trans -esterification process which is carried out by substitutinf glycerol groups by methyl groups in the presence of sodium methoxide as catalyst with the glycerol obtained as a side product. It is this trans-esterification process which is used often in technology today, but, instead of this single step process, sometimes the vegetable oil is hydrolyzed in a first step by, for example, enzymatic hydrolysis or water vapor hydrolysis at high temperature and high pressure to the fatty acids which are then converted to biodiesel by the esterification reaction with methyl alcohol. However this way is not preferred generally preferred by industry.

One of the holistic effective ways for FOG management is biodiesel production by esterification/transesterification of fats. Since FOG is rich in lipids, it is suggested as a cost-effective feedstock for biodiesel, which overcomes many economic disadvantages associated with the utilization of other feedstocks. FOG possesses various ranges of lipids and FFAs, with different biodiesel conversion technologies showing specificity towards the type of raw material for effective conversion. Thus, not all FOG constituents can be effectively converted into biodiesel using a single technology. For instance, only TAGs are highly preferred raw material for conventional transesterification to attain the maximum biodiesel yield. However, some sources of FOG may contain up to 90% of FFAs which hinders the transesterification reaction [54,55,56,57].

In this review we mostly focused on conversion of FFAs in fats, oils and grease (FOG) of wastewater, very little is known about FOG discharged at household level. To address this shortcoming, following a year-long monthly collection of household waste, FOG production was calculated at 2.3 kg/year per household, equivalent to 0.8 kg/year per capita. In the United Kingdom, these numbers translate to an annual estimated household FOG production of 62,380 tonnes. Physico-chemical characterization of household FOG showed promising results for biodiesel production [54]. It can be summerized from Table 2 and 3 that the use of FOGs for biodiesel production also resolves the problems related to their large emissions and complex contamination to the environment. Unfortunately, as discussed above FOGs normally contain large amounts of free fatty acids (FFA), which readily react with alkaline catalysts via saponification, thus lowering the biodiesel yield. Usually, a pre-esterification step is carried out to firstly convert FFAs to FAME with a homogeneous acid catalyst, and then transesterification is performed with alkaline catalyst. However, direct in situ transesterification refers to simultaneous conversion of FOG into biodiesel that was recently discussed as an alternative route to overcome the two-step conversion (See Figure 3). The simultaneous conversion involves the reagents, catalyst and oil mixed directly without prior extraction [20,59].

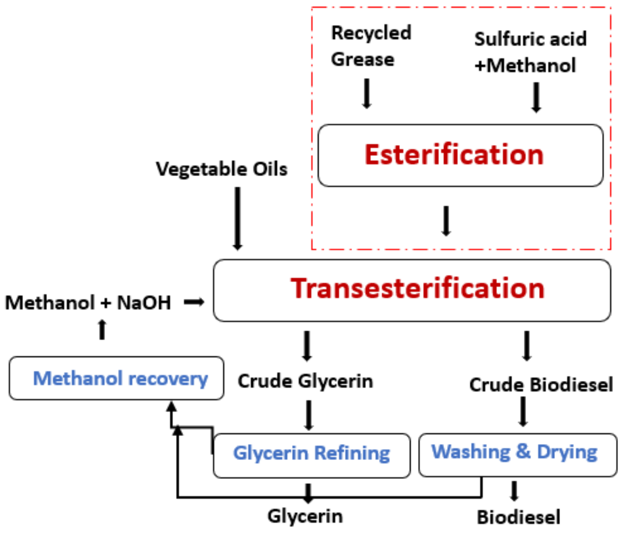


Figure 3 : In situ esterification and transesterification reaction via acid/base catalyst.

The skipping of the extraction step results in significant reduction in the energy consumption and total cost, as well as reduction of physical footprint [60]. Few studies have been performed to explore the feasibility of biodiesel production by the application of in situ transesterification [61,62]. For example, the work done by Dehghani S. and Haghighi M. is shown in Figure 4, which is sumerizes the esterification and transesterification reaction of FOG constituents for FAMEs formation. Si/Ce was used as a nanocatalyst and enhanced the conversion rate of the waste cooking oil into biodiesel significantly (Fig4B) [55] to about 94.3%. At the end of the seventh cycle the biodiesel conversion dropped to 88.7% con version suggesting that the nanocatalyst could be re-used[55]. According to an early investigation conducted by Tu Q. et. al., [62], the optimum operating conditions for in situ transesterification of FOG were 20% H_2SO_4 and 10 :1 methanol : FOG at 65 °C for 7 h, whereby 85.43% of FOG in the raw sewer grease was converted to biodiesel.

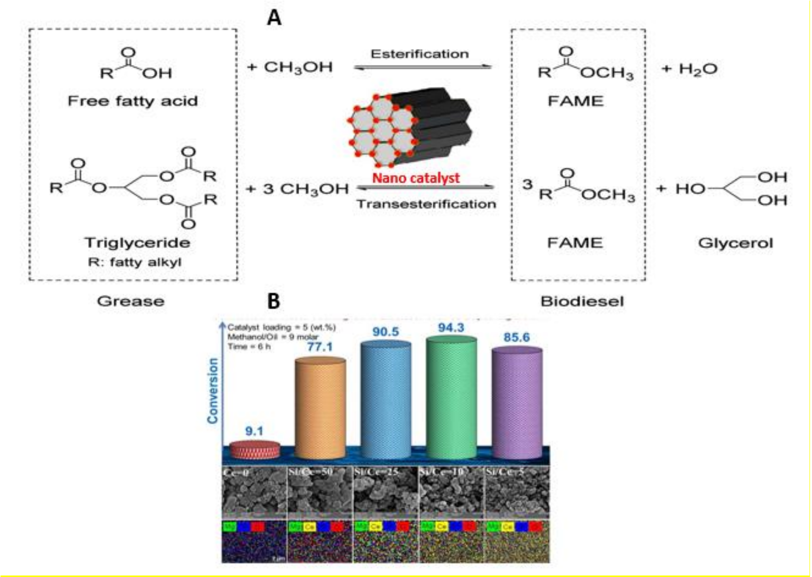


Figure 4 : The esterification and transesterfication reaction for fat, oil, and grease (FOG) conversion into biodiesel (A) and conversion efficieny of yellow grease into biodesel using different molar ratios of Si/Ce (0,5,10,25, and 50) (B) [55].

In addition, Abbaszaadeh et al. [56] esttimated the effectiveness of the thermally induced simultaneous esterification/transesterification of FOG samples nto FAMEs through typical homogeneous acid (e.g., H_2SO_4) catalyzed reactions. Conventional H_2SO_4 catalyzed reaction produced FAMEs with 27.7% (from FOG-high) and 9.2% (from FOG-low) yields. These results indicated that itw as difficult to convert the FOG to FAMEs by the conventional catalyzed methods [56]. Lee J. et al., also reported the thermally induced esterification/ transesterification reaction at 340 °C for samples derived from FOG-high and FOG-low. The highest total FAME yield for FOG-high reached 83.4% at 380 °C at a methanol/feedstock ratio of 20. A further increase in temperature from 380 °C to 390 °C led to a decrease in the yield from 83.4% to 78.7%. In contrast the highest FAME yield for FOG-low was 74.1% at 350 °C at the same methanol/feedstock ratio of 20. Again an increase in temperature from 350 °C to 390 °C led to a decrease in the yield from 74.1% to 59.3%. They suggested that only 83.4% of the initial masses of FOG-high and 74.1% of FOG-low could be converted into FAMEs. FOG-high contains lipids (85.2 wt %), FFAs (11.6 wt%), and impurities (3.2 wt%), and FOG-low contains lipids (76 wt%), FFAs (9.9 wt%), and impurities (14.1 wt%). Impurities are not converted into FAMEs, meaning that they remain after the thermally induced simultaneous esterification/transesterification process. Taking into account the amount of impurities in the feedstock, the total FAME yield from FOG-high and FOG-low would be 86.2% and 86.3%, respectively. Their observation suggested that thermally induced FAME production can be achieved via a single step by combining esterification and transesterification without removing impurities in FOG [20].

The high lipid content contained in waste spent coffee grounds (SCG) was converted to biodiesel through an in situ transesterification method by Tarigan J. Br., and his colleagues[38]. A new approach reactive extraction soxhlet (RES) method of simultaneously extracting and converting lipid from wet SCG biomass to biodiesel in a single-step process at a mild reaction temperature and short reaction time was proposed. Homogeneous sulphuric acid or sodium hydroxide with a concentration of 0.75 M were used as catalysts. The FA to FAME conversion efficiency was more than 90% using sodium hydroxide in methanol with hexane as co-solvent and a ratio of 1 : 2 and 30 min reaction time. The FA extraction efficiencies averaged 58.1 mol% ranging from 48.6–78.1 mol% [38]. The new approach of situ transesterication of wet SCG using RES method resulted in lower energy consumption and reaction time compared to the two-step method which requires a separate extraction and transesterication process [38]. In addition, Suryani A. et al. [57] developed an in situ biodiesel transesterification production process using the residual oil from spent bleaching earth (SBE). The stirring speeds applied were 650 rpm and 730 rpm, and the reaction time varied from 60, 90 and 120 minutes. The combination of 730 rpm stirring speed for 90 minutes transesterification resulted in the best biodiesel characteristics with the yield of 85%, a specific energy of 6,738 kJ/kg and a heater efficiency of 48% [57]. Endalew A. K. et. Al. [48]

investigated mixtures of solid base (CaO and Li-CaO) and acid (($Fe_2(SO_4)_3$) heterogeneous catalyst for single-step simultaneous esterification and transesterification of highcontent free fatty acid (FFA) containing Jatropha curcas oil (JCO) by]. The reaction conditions used were: 60 °C reaction temperature, 3 h of reaction time, 6 :1 molar based alcohol to oil ratio, 5 wt. % catalyst (based on the amount of oil) and an agitation speed of 300 revolutions per min (rpm). Adjusting the CaO : $Fe_2(SO_4)_3$ weight ratio to 3 :1, the FAME yield was 93.37%, while for the Li-CaO catalyst gave a FAME yield of 96% with the same ratio [48].

Later, a new method for waste grease extraction (WGE) was developed, where yellow grease was mixed with raw sewer grease (3.15:1, w/w) at 70 °C for 240 min [63]. During the process, 100% of the FOG in the sewer grease was dissolved/extracted into the liquid yellow grease phase, which separated into two phases with the upper layer containing the FOG (Fig.5). This extraction method resulted in FFAs content increasing from 2.68 wt% in the yellow grease to 8.48 wt% in the extracted FOG, which can be converted directly into biodiesel by in situ transesterification. Using WGE for in situ conversion of FOG into biodiesel has several advantages comparing to the conventional methods. WGE avoids the drying of raw sewer grease that is necessary for many other conversion techniques including in situ transesterification. In addition, using yellow grease for WGE is cost-effective when compared with other techniques used for FOG separation from sewer grease, such as centrifugation. In situ transesterification contains fewer steps compared to other conversion methods and can achieve satisfactory results with FFAs-rich feedstocks. Therefore, it might reduce the complexity and capital investment of FOG conversion. However, methanol and H_2SO_4 inputs are significantly higher for in situ transesterification due to mass transfer limits, even though most of the methanol is recovered after conversion. Therefore, future research is needed in order to improve WGE and in situ transesterification through enhancement of extraction and conversion rates, respectively [63].

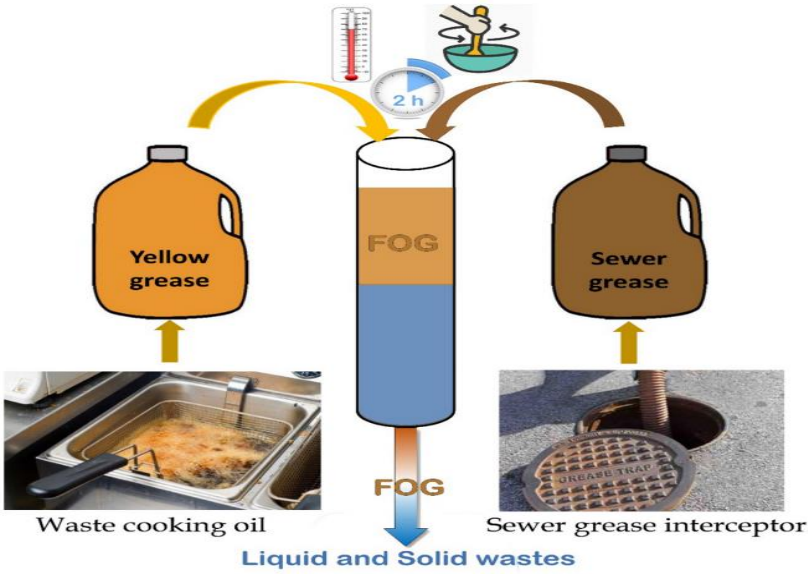


Figure 5 : Solvent-free extraction of waste grease for separation of fat, oil, and grease (FOG) from sewer system.

Moreover, Harvianto G. R. and Ulfasha H. N., [58] firstly performed the esterification (pretreatment) using the methanol : FOG ratio was 0.09 (v/v) at 70 °C for 180 min with 1.2ml of 98% H_2SO_4 (10 wt% of FFA). The amount of conversion in the esterification reaction was shown by the acid value at the end of the reaction. The lower the acid value the greater the conversion with the authors achieving a low value of 0.68 mg KOH/g acid. This was then followed by the transesterification reaction which was carried out with a methanol : FOG ratio of 0.26(v/v) at 70 °C for 30 min with 2.55 g of KOH catalyst [58].

4. Lipid extraction from Biodiesel Feedstock

Brown grease obtained from a wastewater plant was heated to separate biosolids, debris, and oil from the wastewater by decantation. Alternatively, the crude brown grease was screened to remove large debris, melted to separate the water from the biosolids and most of the biosolids, which settled to the bottom, and the wastewater screened again to remove any remaining biosolids. This brown grease still contained significant amounts of water, which was removed by azeotropic distillation with toluene, so that the toluene content of the brown grease generally did not exceed 5wt. % [7].

A novel direct liquid-liquid lipid extraction method for both sewage and petrochemical industry WWTP sludge’s was investigated (see Fig 3). This method did not require expensive sludge dewatering/drying steps compared to the standard drying procedure involved in lipid extraction. Higher lipid and biodiesel yields resulted for petrochemical industry WWTP sludge samples than that obtained by standard drying method. From an economy point of view, liquid- liquid lipid extraction method may be preferred as it eliminates dewatering/drying steps, contributing to 50% of the whole biodiesel production cost [32].

The study explored an alternative method compared to common sludge drying methods (standard method) for lipid extraction, which was called the direct sequential liquid–liquid extraction, in a batch mixer–settler reactor at room temperature, using hexane as a solvent. The optimised direct liquid–liquid extraction of lipids from municipal sewage sludge for biodiesel production, recovered 91% of the lipid fraction from the primary sludge after three extractions. The optimised extraction gave slightly higher lipid content (27w/w%, dry sludge) than the standard method (25%, dry sludge). The proposed alternative, liquid–liquid extraction using hexane, is feasible and compares well with the classical methods [64].

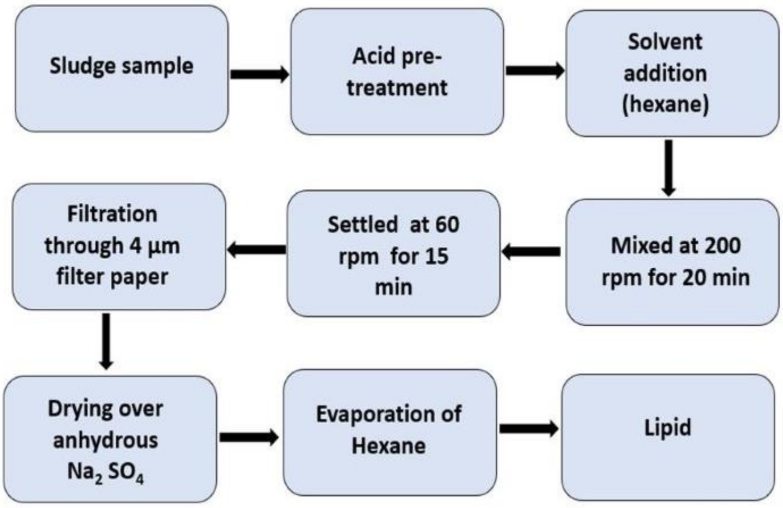


Figure 3 : Direct liquid-liquid lipid extraction of sludge wastewater [32, 64].

Different organic solvents have been used for the simple extraction of FOGs from dewatered grease trap waste (GTW). The raw GTW is first dried in an oven at 110 °C for 24h to 48h until the moisture content of the sample dropped below 5w/w%. FOGs were extracted using different solvents such as ; hexane (HEX), diethyl ether (DEE), and a mixture of hexane - diethyl ether (HEX-DEE). The results showed that the extraction yield increased using the extraction solvent in the following order : DEE > HEX-DEE > HEX. Approximately 88% of FOGs were extracted after two -three extractions [39]. Another study used 200 ml of a mixture of co-solvent methanol, hexane and acetone with different ratios, at 50 °C for 4h to extract lipid from scum, primary and secondary sludge (dry sludge), with sequential extractions using recovered solvent fraction performed three times. It was also found in the study that the neutral lipid was dominant in scum sludge and the maximum lipid yield accounted for one-third of the dried scum sludge when the extraction was performed with the co-solvent (methanol, hexane) containing a high percentage of hexane (60%). Scum sludge achieved the greatest lipid yield (33.3%) compared with primary and secondary sludge which managed to achieve yields of 27.0% and 16.9%, respectively [65].

A solvent-free approach to extract the lipid fraction from sewer grease (SG) for biodiesel production had been used. Waste cooking oil (WCO) was used as the solvent for sewer grease extraction, under optimal condition which were as follows ; 3.2:1 WCO-SG ratio (wt. /wt. %), 70 °C and 240 min. Lipid extraction efficiency from sewer grease was over 90% after two to three sequential extractions reusing WCO solvent [66].

5. Heterogeneous catalysis in the Esterification of fatty acids

The emphasis on environmental protection, as industrial and economic growth gave birth too many forms of pollution threatening human health and earth ecosystems, resulted in the growth of environmental catalysis. Recently, focus has been centered on the use of heterogeneous catalysts due to their properties ; low cost, recoverable and reuse able, easily available, less waste generation, as well as generally environmentally friendly. Esterification of fatty acids with short chain alcohols is very important as this can contribute to the production of biodiesel. Notably, acidic ion exchange resin Amberlyst-15, Amberlyst- 46, Amberlyst-70, Amberlyst-35 and Amberlyst-16 which is an effective, cheaper, and green heterogeneous catalyst and have been widely established for esterfication of free fatty acid. Ion exchange Amberlyst types bead catalyst have high activity towared esterifcation process, due to having high surface area, macroporous pore size active surface (SO_3H) group exhibiting strong acid functionality, allowing good accessbilty of the substrates and contact with the protonated group, [24,25,27,26, 67,68,69, 70]. For example, Boz N. et al. [67] used Amberlyst 15 and modified Amberlyst 15 with optimum reaction conditons of methanol to oil molar ratio

12 :1, 65°C ,3 wt. % catalyst and reaction duration of 540 min to give the highest biodiesel yield of (78 ± 3.39%). Zhang et al. [68] used Amberlyst-15/Poly (vinyl alcohol) membrane as a bifunctional catalyst for obtained high quality biodiesel (98% conversion) from waste cooking oils (WCO), with molar ratio of alcohol to oil 2.5 :1, 15wt. % of catalyst, 65 °C and 120min of reaction time [67]. He proposed the mechanism of esterficaiton reaction over Amberlyst-15 which is discussed in section 6. Also Petechoongsakul et al. [69] observed highest esterification conversion of free fatty acid from waste food oil (WFO) approximately (99.87%) over Amberlyst-15, with molar ratio of alcohol to WFO 4.0 :1, 5wt% of catalyst, using a high reaction temperture of 247-273 °C [69]. Table 4 describes a variety of different types of heterogeneous catalysts and reaction conditions which have been used in the esterification of long chain acids.

Table 4 Heterogeneous catalysis for the esterification of long chain fatty acid (model compounds)

Long chain fatty acid	Catalyst	Reaction conditions	Conversion%	Ref.
Stearic acid	Mesoporous ZrO_2/SiO_2 catalysts prepared with cationic (CTAB) and non-ionic surfactants.	0.4 g of catalyst, reaction time 3hr, ethanol/stearic acid molar ratio of 120 :1, reaction temp. 120 ˚C	76.9% which reduced to 72.5%after five cycles,	19
Stearic acid	Iron Exchanged Montmorillonite (Fe-MMT K10) catalyst	Stearic acid was heated with either ethanol or methanol at 80 ^{o}C for 3 hrs with 2 g of stearic acid in 100 ml of alcohol and 600 mg of solid catalyst.	68%, with ethanol 78% with methanol	71
Stearic acid	PA/NaY (PA = organophosphonic acid, NaY = NaY molecular sieve) catalyst	2.0 g catalyst, reaction time : 4 h, molar ratio of alcohol to acid : 4 :1 and temp : 95 and 100 ˚C.	69.10%	72
Oleic acid	Co-Ni-Pt/ FAU-type zeolites catalyst	Ethanol to oleic acid molar ratio 6 :1 (50ml = 44.75 g); max Temp 70 °C, reaction time 1.5-2 h, batch and continuous esterification	93% for batch and 89% for continuous process	23
-Lauric acid	Ammonium ferric sulphate-calcium silicate AFS-CS catalyst	Methanol to lauric acid, or methanol to Palm fatty acid distillate (PFAD)	-100% for LA	18

-Palm fatty acid distillate (PFAD)		molar ratio was 15 :1, at temp 65 °C, 2h, 16% AFS-CS catalyst.	-72.6% for (PFAD)	
Oleic acid	1-methylimidazolium hydrogen sulfate, [HMIM]HSO_4, ionic liquid	8 h, 110 ± 2 °C, 15 :1 M ratio methanol/oleic acid and a catalyst dosage of 15 wt.%. 8 h, 110 ± 2 °C, 14 :1 M ratio and a catalyst dosage of 14 wt. %.	95 % 90%	73
Oleic acid	Zinc acetate	Molar ratio of methanol to oleic acid 4:1, 1 .0 wt.% zinc acetate catalyst, under pressure 6.0 MPa & 220 °C.	95%	74
Myristic acid	Sulfated zirconia (SZ) solid acid catalyst	Myristic acid to methanol molar ratio of 1:10, 0.5 wt.% solid catalyst, at 60 ^{o}C after 5 h.	98%, after five cycles reduced to 87%	75
Palmitic acid	H-Y and ZSM-5 zeolites as solid acid catalysts	Methanol to palmitic acid molar ratio 2 :1, 3 µmol of catalyst, at 70°C, reaction time 3h.	100%, promising recyclability	76
Oleic acid	10% and 20% WO3/USY/US zeolites	Methyl acetate to oleic acid molar ratio 10 :1, 10%, 20% cat., 240°C,	79.4 wt% and 80.8 wt%	77
Lauric acid	Ag_1 $(NH_4)_2PW_{12}O_{40}$/UIO-66	Lauric acid to methanol molar ratio 1 :15, 10 wt. % catalyst, 150 °C for 3 h	75%, reduced to 58% on sixth recycle	78
Stearic, oleic, and palmitic acids	Montmorillonite-based clay catalysts (KSF, KSF/0, KP10, and K10)	2 g of FFA, in the presence of 0.2 g of montmorillonite KSF/0 (Cc = 0.1w/w) at 150 °C during 4 h using different alcohols. To have the same flow of alcohol (2 × 10^{-2} mol. Min^{-1}) and therefore a constant molar ratio acid/alcohol, the reactor was charged with different alcohol volumes : 195, 280, 360, 445 and 445 mL for methanol, ethanol, propanol, 1-butanol and 2-butanol, respectively.	97% 84% after three cycles).	79
Lauric acid	Niobic acid, niobium phosphate	Fatty acid (50 mmol), alcohol (500 mmol), 10wt. % catalyst, 120-160°C, 7h.	97%, no loss of activity after 3 cycles	77

6. Esterification reaction parameters

Esters are among the highest volume of industrial organic compounds produced. They are frequently employed in various domestic and industrial processes. Fischer esterification regarded as the most common and widely practiced process of ester synthesis, faces serious limitations of low conversion and high reaction time attributed largely to establishment of equilibrium. Ester hydrolysis, reverse reaction to esterification, starts by supply of a byproduct- water. Several approaches have been developed to avoid equilibrium establishment and to improve overall conversion and rate of reaction, a significant difference exists between the current industrial practices and optimum esterification process/conditions. In the following section, there are the discussion of some of those of reaction parameters should be optmized to make the reaction forward and increase the ester product.

6.1 Effect of molar ratio of FFA to alcohol

Many studies have been carried out on esterification reactions of long chain fatty acids with alcohol. As the esterification reaction is an equilibrium-limited reaction, an excess amount of methanol shifts the reaction equilibrium toward the right. Yet other authors have used excess alcohol to optimize their yield of ester over their catalyst. For example, molar ratio of lauric acid to methanol varied from 1 :3 to 1 :18 has been reported by Zhang Q. et al. [78], the rapid conversion of lauric acid from 46.2 to 75.6% was observed as the molar ratio of acid to methanol increased from 1 :3 up to 1 :15. However, they reported that further increase of the molar ratio led to a slight decrease in the conversion of the lauric acid. Excess methanol was thought to cause dilution of both the lauric acid and catalyst, resulting in reduced product [78]. This phenomenon has been seen in a number of other studies as for example in Ezebor F. et. al., where new catalysts prepared from oil palm trunk (OPT) and sugarcane bagasse (SCB) were used in the synthesis of ethyl palmitate and butyl palmitate. The optimum level of methanol to acid ratio was 18 :1, with further increases in methanol failing to lead to enhancement of catalytic performance, as too large excess could cause dilution of reaction system or even shield palmitic acid molecules from the catalyst active sites [81]. Similar observation was reported by other investigators [82,83,84], where FAME yield increases with increase in methanol/oil molar ratio, but too large excess had no positive effect.

Free fatty acids (FFA) were esterified with anhydrous methanol, using a methanol/oleic acid molar ratio of 20 :1– 80 :1 and 10 :1–114 :1 with a sulphuric acid catalyst concentration of 5% and 10%, respectively. Based on the experimental results, a methanol/oleic acid mole ratio of 60 :1, a catalyst (sulphuric acid) concentration of 5 wt. % and a temperature of 60 ˚C provided a final acid value for the oil lower than 1 mg KOH/g oil within 120 min [85]. Also, the effect of molar ratio of alcohol to acid from 4 :1 up to 8 :1 on stearic acid conversion has been investigated by Liu W. et al., molar ratio of alcohol to acid of 4 :1 provided the best conversion. They explained that a drastic drop of conversion with increased molar ratio of alcohol to acid from 4 :1 to 8 :1 can be attributed to the saturation of the catalytic surface with the alcohol or prevention of nucleophilic attack by shielding protonated alcohol by its own excess [72].

6.2 Effect of concentration and type of catalyst

It has been shown that by increasing the amount of catalyst, the number of acid sites also increases in the esterification of FFAs, which allows accessibility of a greater number of reactant molecules resulting in an increased yield of the ester. The effect of the amount of catalyst in the range of 1-12 wt. % on lauric acid conversion has been investigated by Zhang Q. et al. [78]. A novel solid acid nano-catalyst ($Ag_1 (NH_4)_2PW_{12}O_{40}$/UiO-66) comprising ammonium and silver co-doped $H_3PW_{12}O_{40}$ and zirconium-based metal−organic framework (UiO-66) was used in the conversion of lauric acid. The optimum amount of catalyst was 10 wt. %, and the rate of reaction was slightly increased with further increase of catalyst amount [78]. The effect of catalyst loading from 0.01–0.2% w/w over commercial acid clays (KSF, KSF/0, KP10, and K10) for conversion of stearic acid with ethanol, at 150 °C, for 4 hours has been studied [79]. Ester conversion increased proportionally with the concentration of catalyst ; whereas it was found to be independent of the catalyst concentration above 0.1 %w/w (97% of fatty acid was converted). The results obtained suggest that the initial activity increased with the total number of available active catalytic sites.

The esterification reaction of stearic acid with methanol and ethanol over cation exchanged montmorillonite K10 (MMT K10) was studied [71]. A series of Fe- MMT clay catalysts were prepared by adding 10 g of MMT K10 to 0.25, 0.5, 0.75, 1 M aqueous solution of Fe $(NO_3)_3$ at 80 ^oC for 8 h. These iron exchanged MMT K10 (Fe-MMT K10) clays were used to esterify stearic acid. The increase in ion concentration affected the percentage of conversion maximising at 0.75 M Fe-MMT K10, and then slightly decreasing for 1M Fe-MMT K10. High stearic acid conversion of 75% was obtained for 0.75 M iron concentration [71].

6.3 Effect of reaction temperature and alcohol types

The effect of reaction temperature was studied on esterification reaction of long chain fatty acids. As most of these long chain fatty acids are insoluble in methanol at room temperature, their solubility increases with temperature resulting in higher conversion as the higher temperature facilitates the protonation of the carbonyl group of the acid and favours the nucleophile attack of methanol on the acid. Many authors investigated the effect of temperature on FFA conversion such as ; a high temperature range from 110 to 160 °C performed on the esterification of lauric acid by Zhang Q et. al., [78]. It was found that there was a gradual increase in the lauric acid conversion on increasing temperature from 110 to 150 °C. However, a slight decrease in lauric acid conversion was observed beyond 150 °C, probably because there was a loss of methanol due to evaporation [78]. Other work on stearic acid showed increased conversion with increased temperature from 90 to 100 °C arising from an increased mass transfer rate. Higher temperatures are known to greatly accelerate reaction rate and improve the mass transfer limitation between reactant and catalyst. However, increase in temperature from 100 to 110 °C reduced stearic acid conversion, whilst conversion slightly changes with further temperature increase from 110 to 140 °C [72]. Their optimum reaction temperature was 100 °C, in order to save the energy of the process, as they didn't notice significant product conversion beyond 100 °C. In contrast, Bassan I. A.L. et. al. [80], found a maximum conversion of 80% for lauric acid esterification with methanol after 2 hr at the higher temperature of 160 °C in batch reactor [80]. The conversion of oleic acid over Amazon flint kaolin (MF9S4) solid acid catalyst increased with increasing temperature from 13.5% at 100 °C to 98.9% at 160 °C [72].

The effect of the different alcohols was evaluated in the esterification of fatty acids catalysed by different type of catalysts. The esterification of lauric acid with the alcohols methanol, ethanol, butanol using niobic acid with niobium phosphate catalyst was studied by Bassan. Reaction conditions were molar ratio alcohol : acid 10 :1, reaction time of 4 hours, catalyst concentration of 10% w/w in relation to fatty acid. For all the alcohols the reaction temperature was selected below the boiling temperature of each alcohol studied. The conversion of lauric acid was less than 35% with methanol and ethanol under atmospheric pressure. The highest lauric acid conversion results were achieved (around 81%) in the reaction with 1-butanol [80]. The esterification of acetic acid with ethanol, butanol and iso-pentanol catalysed by $Nb_2O_5/SiO_2–Al_2O_3$ where it was found that reactivity increased from ethanol to iso-pentanol [86].

In addition, Neji et al., evaluated different alcohols i.e., methanol, ethanol, propanol and butanol in the esterification of stearic acid catalysed by montmorillonite KSF/0 at 150 ^oC for 4 hours using semi-continuous reactor working above the boiling point of water and alcohol. This enabled continuous removal of the water produced which caused a shift in equilibrium towards esterification. In their study butanol which has the higher boiling point of 117.5 ^oC which evaporated at lower rate than the other alcohols at the reaction temperature of 150 ^oC, hence it gave the higher conversion of 99 % [79].

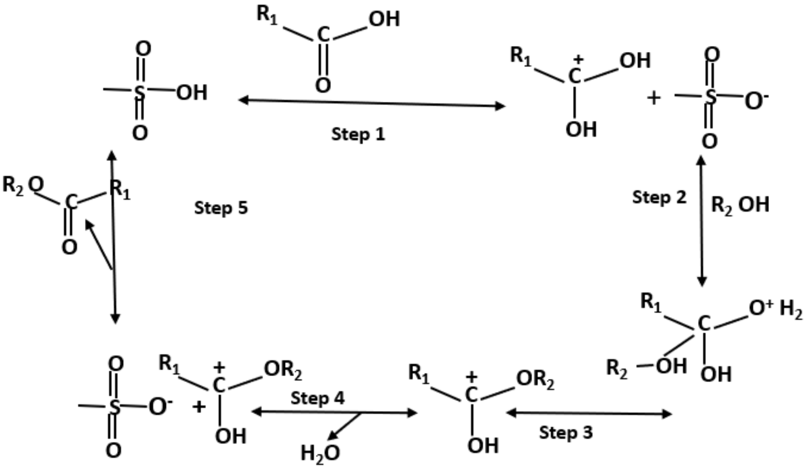
6.4 Effect of reaction time

Reaction time studies are useful in identifying product formation and reactant disappearance, as reported by Liu W. et al., in the esterification of stearic acid. Their results indicate that the esterification reached equilibrium after 4 hours, after which conversion decreases with further increase of reaction time to 7 hours [72]. However, the effect of reaction time in the esterification of lauric acid with 1-butanol has been reported over niobium phosphate catalyst by Bassan I. A.L. et al., in contrast their conversion was higher than 95% after 7 h [80]. In summary, all esterification reaction parameters are co-related to each other. For instance, the reaction time depends on reaction parameters, such as the acidity and amount/type of the catalyst, temperature, the molar ratio of acid to alcohol. For example, if the catalyst amount increases, it means more acid sites are available, and if the reaction temperature is high, the time to reach the equilibrium state is much shorter.

Further examples, the effect of reaction time for the esterification of stearic acid with ethanol and methanol has also been investigated by using iron exchanged Montmorillonite K10 Clay Catalysts. The conversion of stearic acid generally increased with increasing reaction time. In the initial 5 minutes of reaction, the conversion of the steric acid with ethanol was 47 % after which the reaction proceeded rapidly within 40 minutes to achieve a conversion of 65%. Then, the conversion remained almost constant until 180 minutes when it was only slightly increased to 68 %. Using methanol as the alcohol in the conversion of stearic acid to methyl stearate, the conversion exhibited a different reaction profile where in the first 5 minutes conversion of 68 % was achieved which increased over 180 minutes to 78 % [71]. The rate of esterification of oleic acid reached 98.9% on extending reaction time from 30 min up to 240 min using reaction conditions of acid : alcohol molar ratio of 1 :60 at 160◦C, over amazon flint kaolin (MF9S4) solid acid catalyst [87].

7. Mechanism of esterification reaction

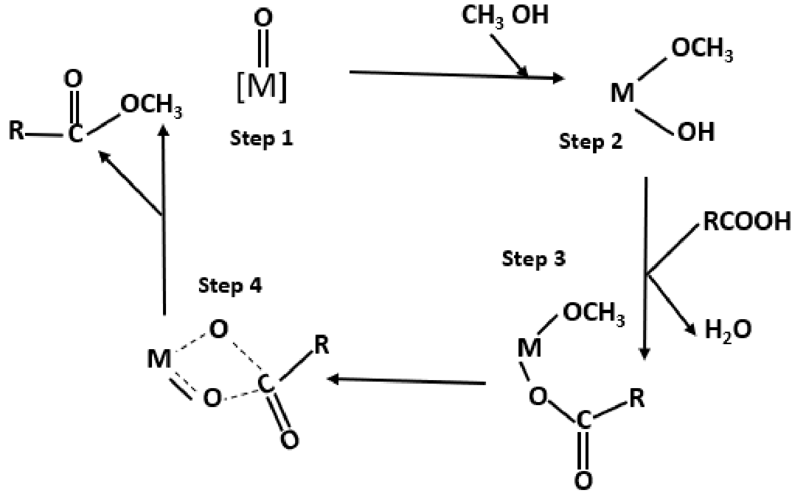
To an organic chemist, the term ester normally means an ester of a carboxylic acid. Replacing the group of a carboxylic acid with the group of an alcohol gives a carboxylic ester (See Fig. 1 Above). The general mechanism of carboxylic acid with alcohol in the presence strong acid such as sulphuric acid involved in five steps include: protnation of carboxylic acid, addition of alcohol, proton transfer, elimenation of water molecule and deportonation of hydrogen ion (See Scheme 1) [88]. Carboxylic acids can be esterified by alcohols in the presence of a suitable acidic catalyst (for example H_2SO_4) as illustrated in Scheme 1. The initial step is protonation of the acid to give an oxonium ion, which can undergo an exchange reaction with an alcohol to give the intermediate, and this in turn can lose a proton to become an ester. Each step in the process is reversible but in the presence of a large excess of the alcohol, the equilibrium point of the reaction is displaced so that esterification proceeds virtually to completion. However, in the presence of water, which is a stronger electron donor than are aliphatic alcohols, formation of the intermediate is not favoured and esterification will not proceed fully [89].



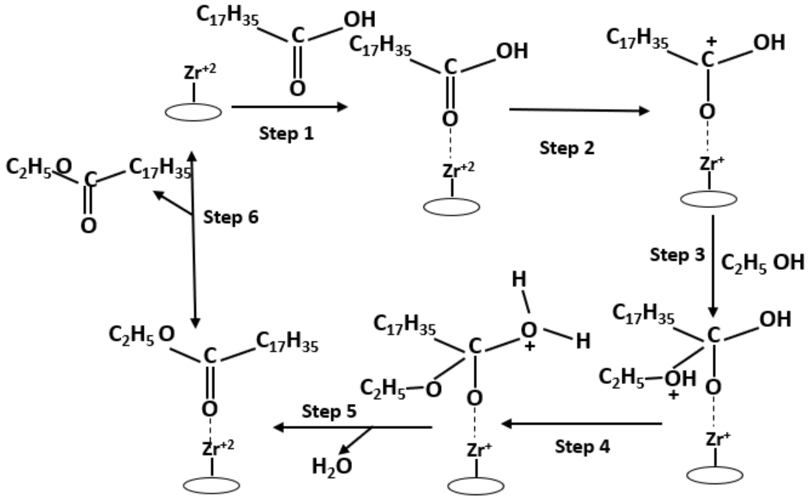
Scheme 1: Esterfication reaction mechanism of carboxylic acid with alcohol.

The mechanisim of esterification reaction has been proposed over heterogenous acidic catalyst by several reseachers. The feasible procedure for recovery and reuse besides the high yields of biodiesel suggest that the heterogenous acid catalyst are potentially useful for biodiesel production. Those authors proposed a mechanism of the soild catalytic action as described in Scheme 2, 3 & 4 [90,91,92,93,94]. The authors suggested that the molecules of fatty acid adsorbed on the surface of catalyst, due to interaction between metal cation present in the catalyst oxide (Lewis acid, M^{2+}) and electrons of the carbonyl group oxygen atom (base). So, the density of positive charge of carbonyl carbon increase due to this interaction and the nucleophilic attack takes place by electrons pair of the alcohol hydroxyl group. The resulting intermediate eliminates a water molecule and the ester formed. Finally, the surface of catalyst is free to participate in the next catalytic cycles [90-94].

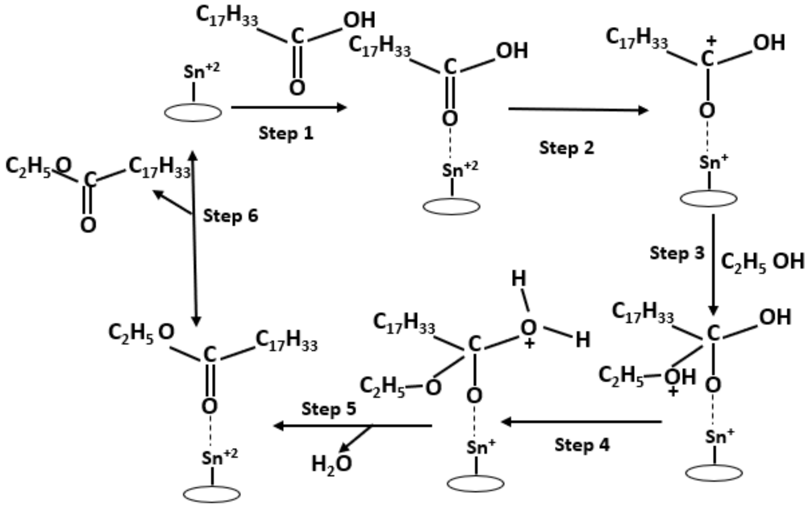
The mechanisms of the acid catalysed esterification involving heterogeneous catalysts is given by the general mechanism of scheme 2. Schemes 3 and 4 have also been added to show that two different solid acid catalysts using two different fatty acids follow the same general mechanism of scheme 2, whilst showing two more steps describing two additional mechanistic steps.



Scheme 2: Proposed mechanism for the esterification of fatty acids catalyzed by Lewis acid metal oxides [90, 91].



Scheme 3: Proposed mechanism for the esterification of stearic acid catalyzed by Lewis acid metal oxides (ZrO_2 supports on Al_2O_3, Fe_2O_3, TiO_2 and SiO_2) [92].



Scheme 4 : Proposal of a mechanism for the ester formation catalyzed by $SnCl_2/M_xO_y$ (M = Zr or Nb ; x=1 or 2 ; y=2 or 5) in the oleic acid esterification into ethyl oleate [93, 94].

In summary, the mechansim of heterogenous catalysis takes place over the surface of the metal supported catalyst, via several steps such as : Diffusion of the reactants through a boundary layer surrounding the catalyst particle ; intraparticle diffusion of the reactants into the catalyst pores to the active sites ; adsorption of the reactants onto active sites, surface reactions involving formation or conversion of various adsorbed intermediates, possibly including surface diffusion steps ; desorption of products from catalyst sites ; Intraparticle diffusion of the products through the catalyst pores ; diffusion of the products across the boundary layer surrounding the catalyst particle [95]. In contrast, the mechanism of homogeneous catalysis occurs in the following steps : protonation of the carbonyl oxygen, addition of the alcohol, proton transfer, elimination and deprotonation.

8. Challenges and Sustainability

The sustainability for developing the proposed FOG waste- biodiesel production has three main pillars : the environment, economy, and society. For the environmental aspects, the use of a low cost feedstock such as FOGs in wastewater effluent makes use of a waste commodity. The optimization of reaction parameters in particular reduced temperature and use of organic solvents (although these can be reclaimed) can achieve the conversion of FOG up to at least 94%. From economic aspects, FOGs are a potentially sustainable biodiesel feedstock due to their high FFA content, which on esterification not only produces biodiesel but also profitable side products of glycerol and K_2HPO_4 in an enviromentally eco-friendly stystem [21].

There is potential of using and recycling a low cost feedstock such as FOGs which causes severe environmental pollution, and blockage of sewers in developed countries such as the UK and USA. Also, fatty acid methyl esters (FAMEs) /biodiesel the outcome of esterification is a renewable energy with low carbon dioxide emission, zero or lower sulphur content and lower particulate matter emission especially of concern in the transportation sector. Nowadays, the global use of biodiesel as fuel is approximated at 10% and the aim is to increase this as a cleaner alternative energy for fossil fuel and traditional petroleum energy particlualy in transportation sector by 2050. To ensure social sustainability, a new framework of FOG-management could effectively cope with the related environmental problems and reduce the human environmental impact.

A challenge to the use of FOG$_S$ as source for biodiesel production is that the composition of FOGs varies substantially among different sources which leads to inconsistency in FOGs characteristics causing variations in biodiesel characteristics, the production cost, and the optimum operation conditions. Another challenge is that it is difficult to develop an effecient heterogenous catalytic system to tranform feedstock based -FOGs to biodiesel production. Heterogeneous catalysts can avoid the use of corrosive liquid acids and bases with associated storage and handling problems.

On the one hand, biodiesel production of FOGs is more difficultas it requires more steps than when processing pure oils, e.g. Purification of FOGs (filtration, purfication and water removal) and also requires an esterification step of the free fatty acids before the transesterification reaction which produces the biodiesel. On the other hand, it is very desirable to transform FOGs into fuel rather than using fresh oils, that could be otherwise be used in the food industry. If heterogenous acid catalysts could be as efficient in the esterification of FOGs as it is with fresh oil such as vegetable oil, this would motivate its use in industry, even if catalyst production increases some costs but, at the same time, decreases the associated costs of catalyst separation and purification after the reaction and indeed canenable catalyst re-use. Future steps should include an analysis of heterogenous catalyst usage in the transformation of FOGs into a biofuel.

9.Conclusion

This review has shown that the esterification of high free fatty acid lipid feedstocks from wastewater containing FOGs is an alternative route to biodiesel production as a renewable energy is possible. Based on this literature review, numerous studies have been done on the esterification of free fatty acids and their transformation into fatty acid methyl esters (FAMEs) which is the main constituent of biodiesel. The yield of biodiesel depends on a number of parameters ; such as catalyst concentration, catalyst type, and molar ratio of reactants, reaction temperature, and reaction time and optimization of these reaction conditions.

There are four primary factors affecting the yield of biodiesel, i.e. alcohol quantity, reaction time, reaction temperature, and catalyst concentration. To ensure a high yield of FAMEs, the molar ratio of alcohol to fatty acid should be increased to between 6 :1 up to 20 :1 with the use of an acidic catalyst. For used cooking oils or for oils with a high percentage of free fatty acids, a higher molar ratio is needed for the acid-catalysed reaction. Whilst the conversion rate of fatty acid esters increases with reaction time the yield of the biodiesel product reaches a maximum at an optimal reaction time. Higher reaction temperature can decrease the viscosity of oils, enhancing the reaction rate. The optimal temperature ranged between 90 °C and 160 °C for heterogeneous catalyst and in the range of 60 °C to 65 °C for homogenous acidic catalyst, depending on the amount of free fatty acids that the oil contains. The optimal condition of catalyst concentration is about 6 wt. % up to 10wt. % for heterogeneous solid acidic catalysts and between 3 to 5 %v/v for H_2SO_4 which is the most commonly used catalyst. Therefore, all reaction parameters are co-related to each other and all of them have significant influence on the reaction, therefore all parameters have to be optimized.

With increasing concern over global warming, it is foreseeable that biodiesel usage would continue to grow at a fast pace. This will trigger the development of more sophisticated methods of biodiesel production and refining to cope with the increasing market demand.

Acknowledgement

This work is supported by funding from the co-sponsors Daphne Jackson Trust, Society of Chemists in Industry (SCI) and Royal Society of Chemistry (RSC), and hosted at De Montfort University, Leicester. I also thank for Dr Pang for his revision.

10.Reference

[1] Bora A. P., Gupta D. P. and Durbha K. S., Fuel, 259 (2020), 116262.

[2] Tarigan J. Br., Ginting M., Mubarokah S.N., Sebayang F., Karo-karo J., Nguyen T. T.,Ginting J. and Sitepu E. K., , RSC Adv. , 9 (2019), 35109.

[3] Kouzu M., HIdaba J.S., *Fuel, 93(*2012), 1-12.

[4] Semwal, S., Arora, A.K., Badoni, R.P. & Tuli, D.K.,Bioresour. Technol*., 102* (2011), , 2151-2161.

[5] Srivastava N., Srivastava M., Gupta V. K., Manikanta A., Mishra K., Singh S., Singh S., Ramteke P. W. And Mishra P. K., 3Biotech, 8 (2018), ,245.

[6] Dimian, A. C. and Kiss, A. A. J., Clean. Prod., 239 (2019), 2-42.

[7] Bashira M.J.K., Wong L. P., Hilaire D. St., Kim J., Salako O., Jean M. J., Adeyemi R., James S. , Foster T., Pratt L.M, J. Environ. Chem. Eng., *8*(4), (2020), 103848.

[8] Abomohra Abd El-F., Elsayed M., Esakkimuthud S., El-Sheekh M., Hanelt D., Prog. Energy Combust. Sci., 81(2020), 100868.

[9] Marchetti J.M. and Errazu A.F., *Biomass Bioenergy*, *32* (2008), , 892-895.

[10] Tran N., Tisma M., Budzaki S., Hessel V., Ind. Eng. Chem Res., 60(5), (2021),

[11] Cankci M., Bioresour. Technol., 98 (2007), 183-90.

[12] Montefrio MJ., Xinwen T., Obbard JP., Appl. Energy, 87 (2010), ,3155-61.

[13] Suto P., Gray D., Larsen E. Hake J., Proc. Water Environ. Fed., 2006 (2008), ,858-79.

[14] Parry DL, Vandenburgh S, Salerno M., 2008 (2008), 1045-62.

[15] Yousfi M., Bombarda I., Hamia C., Djeridane A., Stocker P., Gaydou E., Mediterr J Nutr Metab 2(2009) ,197–203.

[16] Sankaran R., Show P. L., and Chang J.-S., *Biofuels Bioprod. &Biorefin., 10,(*2016), 896–916.

[17] Daud N. M., Sheikh Abdullah S. R., Abu Hasan H. and Yaakob Z., *Process Saf. and Environ. Prot., 94,(2015),* , 487-508.

[18] Ganesan S., Nadarajah S. , Chee X. Y. , Khairuddean M. , Teh G. B., *Renewable Energy, 153(*2020), , 1406-1417.

[19]Mahmoud H. R. , El-Molla S. A., Ibrahim M. M., Renewable Energy, 160 (2020), , 42-51.

[20] Lee J., Jung J-M., Park C., Jeon B-H., Wang C-H., Lee S-R., and Kwon E. E., J. Cleaner Prod., 168,(2017), 1211-1216.

[21] Taipabu M. I., Viswanathan K., Wu W., Nagy Z. K., Chem. Eng. J. 424 (2021) 130199

[22] Ibrahim M. M., Mahmoud H. R., El-Molla S. A., Catal. Commun.,122(2019), , 10–15.

[23] Alismaeel Z .T., Abbas A. S., Albayati T. M., Doyle A. M. , *Fuel, 234 (2018)*, 170-176.

[24] Leyva F., Orjuela A., Miller D. J., Gil I., Vargas J. and Rodríguez G., Ind. Eng. Chem. Res., 52, (2013), 18153−18161.

[25] Banchero M. and Gozzelino G., Energies, 11 (2018),1843.

[26] Ilgen O., Fuel Process. Technol., 124, (2014), 134–139.

[27] Alhassani M. H., Al-Jubouri S. M., Noori W. O., Al-Jendeel H. A., International Journal of Engineering (IJE), IJE TRANSACTIONS B : Applications ,31(8), (2018), 1172-1179.

[28] Naik B. D., and Udayakumar M., Mater. Today : Proc., 46 (2021), 9855–9861

[29] Saravanan K., Tyagi B., Shukla R. S., Bajaj H C., Fuel, 165, (2016), 298–305.

[30] Saravanana K., Tyagi B., Shuklaa R.S., Bajaj H.C., Appl. Catal. B : Environ., 172–173, (2015), 108–115.

[31] Thushari I and Babel S. (2018). Bioresou. Technol., 248 , 199-203.

[32] Babayigit E., Atik Alper D. and Erdincler A., Waste Biomass Vaporization,9(2018), 2471-2479.

[33] Olkiewicz M, Fortuny A, Stüber F, Fabregat A., Font J., Bengoa C., *Fuel, 141(2015)*, 250–257.

[34] Qi J, Zhu F, Wei X, Zhao L, Xiong Y, Wu X, Yan F. ,Waste Manage.,49(2016), 212–220.

[35] Olkiewicz M., A Fortuny., Stüber F., Fabregat A., Font J., Bengoaa C., Procedia Eng., 42,(2012), 634 – 643.

[36] Mondala A., Liang K., Toghiani H., Hernandez R., French T., Bioresou. Technol., 100 (2009), 1203–1210.

[37] Pastore C., Lopez A., Lotito V., and Mascolo G., *Chemosphere,92*(6)*,* (2013), 667-673.

[38] Tarigan J. Br., Ginting M., Mubarokah S.N., Sebayang F., Karo-karo J., Nguyen T. T.,Ginting J. and Sitepu E. K., RSC Adv., 9 (2019), 35109.

[39] Tran N. N., Ho P. Q., Hall T., McMurchie E. J., Ngothai Y., J. Multidiscip. Eng. Sci. Studi., 3(2017), 1853-1859.

[40] Farooq M., Ramli A. and, Subbarao D., J. Cleaner Prod., 59(2013), 131-140

[41] Liang X., Xiao H., Qi C., Fuel Process. Technol., 110(2013), 109-113.

[42] Fatah M. A., Mansour M. S. and Fouad Y.O., Int. J. Chem. Biochem. Sci.,9 (2016), 33-43.

[43] Istadi I., Prasetyo S. A. and Nugroho T. S. ,Procedia Environ.l Sci., 23(2015), 394 – 399

[44] Feyzi M. and Norouzi L., Renewable Energy,94(2016), 579–586.

[45] Hu S., Guan Y., Wang Y., Han H., Appl. Energy, 88(8), (2011), 2685–2690.

[46] Reddy A.N.R., Saleh A.A., Isalm M.S., Hamdan S. and Maleque M. A., Energy Fuels, 30(1) (2016),334–343.

[47] Prabu M., Manikandan M., Kandasamy P., Kalaivani P. R., Rajendiran N., and Raja T., ACS Omega,4 (2019), 3500−3507.

[48] Endalew A. K., Kiros Y. and Zanzi R., Energy, 36 (5) (2011), , 2693-2700.

[49] Baskar, G. & Soumiya, S., Renewable Energy, 98(C),(2016), 101-107.

[50] Widayat W., Darmawan T., Hadiyanto H. and Ar Rosyid R., J. Phys.: Conf. Ser., 877 (2017), 012018.

[51] Ozbay N., Oktar N., Tapan N. A., Fuel 87 (2008) 1789–1798.

[52] Cabral N. M., Lorenti J. P., Plass W. & Gallo J. M. R., Front. Chem., 8(2020), 305.

[53] Patino Y., Faba L., Díaz E. & Ordonez S., J. Water Process Eng., 44 (2021), 102335

[54] Collin T., Cunningham R., Deb M., Villa R., MacAdam J., Jefferson B., Water and Environ. J., 1–10 (2021), Available from : https://doi.org/10. 1111/wej.12744

[55] Dehghani S. and Haghighi M., Waste Management 95 (2019) 584–592.

[56] Abbaszaaseh A., Ghobadian B., Omidkhah M. E., Najafi G., Energy Conv. Manag., 63(2012),138-148.

[57] Suryani A., Mubarok Z., Suprihatin, Romli M. and Yunira E. N., IOP Conf. Series : Earth Environ. Sci. 65 (2017) 012040.

[58] Harvianto G. R. and Ulfasha H. N., Int. J. Environ. Bioener. 2012, 3(1): 56-66.

[59] Son J., Kim B., Park J., Yang J., Lee J. W., Bioresour Technol, 259(2018), 2085-8.

[60] Aboelazayem O., Gadalla M., Saha B., Renew Energy, 124(2018), 144-54.

[61] Choi O.K., Song J.S., Cha D. K., Lee J. W., Bioresour Technol, 166 (2014), 51-56.

[62] Tu Q., University of Cincinnati, 2015. https://doi.org/oai:etd.ohiolink.edu:ucin1448.

[63] Tu Q., Wang J., Lu M., Brougham A., Lu T., Waste Manag., 54(2016),126-30.

[64] Olkiewicz M., Caporgno M. P., Fortuny A., Stüber F., Fabregat A., Font J. and Bengoa C.,Fuel Process. Technol., 128 (2014) , 331–338.

[65] Wang Y., Sha F., Xiaojuan B., Jingchan Z. and Siqing X., Waste Manage., Part A 47 (2016), 91-97.

[66] Tu, Q., Wang J., Lu M., Brougham A. and Lu T., Waste Manage., 54(2016), 126-130.

[67] Boz N., Degirmenbasi N., and Kalyon D. M., Appl. Catal. B : Environ., 165 (2015) 723–730.

[68] Zhang H., Tiana F., Xu L., Peng R., Y Li Y., Deng J., Chem. Eng. J., 388 (2020) 124214.

[69] Petchsoongsakul N., Ngaosuwan K., Kiatkittipong W., Aiouache F., Assabumrungrat S., Energy Convers. Manage. 153 (2017) 493–503.

[70] Ozbay N., Nuray Oktar N., Tapan N. A., Fuel, 87 (2008) 1789–1798.

[71] Almadani E. A., Radzi S. M., Harun F. W., Int. J. Appl. Chem.,12(1), (2016), 62-67.

[72] Liu W., Yin P., Liu X., Zhang S., Qu R., J. Ind. Eng. Chem., 21 (2015), 893–899.

[73] Roman F. F., Ribeiro A. E., Queiroz A., Lenzia G. G., Chaves E. S., Brito P,. Fuel, 239 (2019), 1231–1239.

[74] Song C., Qi Y., Deng T., Hou X., Qin Z. , Renewable Energy,35 (2010), 625–628.

[75] Saravanana K., Tyagia B., Bajaja H. C., Indian J. Chem. Sect. A,53(7),(2014),799-805.

[76] Prinsen P., Luque R., González-Arellano C., Microporous and Mesoporous Mater., 262 (2018), 133–139.

[77] Ketzera F., Celante D., de Castilhos F., Microporous and Mesoporous Mater.,291 (2020), 109704.

[78] Zhang Q., Yang T., Lei D., Wang J. and Zhang Y. ,ACS Omega, 5 (22), (2020), 12760–12767.

[79] Neji S. B., Trabelsi M. and Frikha M. H., Energies,2 (2009),1108-1117.

[80] Bassan I. A.L., Nascimento D. R., San Gil R. A.S., Pais da Silva M. I.,Moreira C. R., Gonzalez W. A., Faro Jr A. C., Onfroy T., Lachter E. R., Fuel Process. Technol., 106 (2013), 619-624.

[81] Ezebor F., Khairuddean M., Abdullah A. Z., Boey P. L., Energy ,70(2014), 493-503.

[82] Satyanarayana M, Muraleedharan C. A, Energy 36(4), (2012), 2129-37.

[83] Uzun BB, Kılıç M, Özbay N, Pütün AE, Pütün E. Energy ,44(1), (2012),347-51.

[84] Rasimoglu N, Temur H., Energy, 68(0), (2014), 57-60.

[85] Berrios M., Siles J., Martı´n M.A., Martı´n A., Fuel,86 (2007), 2383–2388.

[86] Braga V.S., Barros I.C.L., Garcia F.A.C., Dias S.C.L., Dias J.A., Catal. Today, 133-135 (2008), 106–112.

[87] Nascimento L. A. S., Tioto L. M. Z., Angelica R. S., da Costa C. E. F., Zamian J. R. and da Rocha Fiilho G. N. Appl. Catal. B-Environ., 101 (2011), 495–503.

[88] Wade JR. L. G., Organic chemistry, Ch. 21 : Carboxlyic acid derivatives, 8th Ed. (2013), USA, 981-1004.

[89] Christie W.W., in Advances in Lipid Methodology – Two, (1993), 69-111, [Ed. W.W. Christie, Oily Press, Dundee].

[90] Silva M.J. D., Cardoso A.L, J. Catal. 2013 (2013) 1–11

[91] Mello V. M., Pousa G. P. A. G., Pereira M. S. C., Dias I. M., and SuarezP. A. Z. Fuel Process. Technol., 92 (1), (2011), 53–57.

[92] Ibrahim M. M., Mahmoud H. R., El-Molla S. A., Catal. Commun. 122 (2019) 10–15.

[93] Cordeiro C. S., Silva F. R. D., Wypych F., and Ramos L. P., “Heterogeneous catalysts for biodiesel production,” Quimica Nova, 34 (3), (2011), 477–486.

[94] Yan S., Salley S. O., and Ng K. Y. S., Appl. Catal. A, General, 353 (2), (2009), 203–212.

[95] Ertl G., Knozinger H., Schuth F., Weitkamp J., Handbook of heterogenous catalysis, 2nd Ed., Vol 1., Ch. 1, P.2, Wiley-VCH.

Bibliography

Dr. Rawaz Ahmed : She received a scholarship from Kurdistan to pursue a Ph. D in heterogeneous catalysis on the dry reforming of methane at bteeside University, UK, which was followed by a 1 year Post Doctoral Fellowship in the hydrothermal conversion of poultry litter for nutrient recovery also at Teesside University. She won first prize for her poster at the Royal Society of Chemistry Conference in March 2011, and this work resulted in a patent application (P136962GB). She then spent 5 years as a lecturer at Kurdistan Institute for Strategic Study and Scientific Research (KISSR). Since October 2021 she is a Daphne Jackson Fellow funded by both the Royal Society of Chemistry and Society of Chemists in Industry (UK) hosted by Professor Katherine Huddersman at De Montfort University, Leicester, UK. Here she is focussing on the application of a heterogeneous catalyst in the esterification/tranesterification of FOGs from wastewater for the production of biodiesel.

Professor Katherine Huddersman is a Professor of Environmental Chemistry at De Montfort University focussed since 1996 on the production, characterisation and applications of a heterogenous modified polyacrylonitrile catalyst which is surface functionalised to enable iron complexation. She has applied this oxidation catalyst to wastewater treatment, disinfection and the production of chemicals. She is the recipient of over £4M of funding from UK governmen.

Reviewer comments

Reviewer #1: This paper reviews the potential biodiesel production by esterification of wastewater containing Fats Oils and grease (FOGs) and investigated the effect of feedstock pre-treatment and process parameters by esterification, including alcohol to oil molar ratio, reaction temperature, reaction time, catalyst amount. Some important point from previous comment has been addressed by the author. However, author has to consider other comments before considering for publication.

1. Amberlyst catalysts in esterification process has been considered in this paper but more detail information related to operating parameters is necessary and included in Table 3 especially for Amberlyst-15 type as frequently used.

The bottom rows of Table 3 have been amended to include a number of Amberlyst catalytic reaction details (Page 13) and further discussion is included in Section 2 page 15. The Amberlyst catalyst and parameters also has been further discussed in section 5 page 23. These sections have been highlighted in yellow.

2. Better to draw carbonyl group in Figure 2 as presented in Figure 1 (O-C=O) instead of -OOC.

The carbonyl group of figure 2 has been re-drawn in the same style as figure 1.

3. More important things is the FFAs content in FOGs is around 15% so only few biodiesel products can be expected and huge number of triglyceride (around 85%) is necessary to considered as main process of biodiesel production from FOGs as feedstock using transesterification. Instead, hydrolysis reaction pathway can be considered to convert triglyceride into free fatty acid and thus, esterification process can be totally selected as a main process of biodiesel production.

So we recommend the author to consider either esterification-transesterification or hydrolysis-esterification reactions pathway for FOGs-to-biodiesel conversion.

A significant section on the describing both esterification-transesterification as well as the hydrolysis-esterification reactions for FOGs conversion to biodiesel has been included in Section 3 and highlighted in green.

4. By considering the comment No. 1 and 3 then it gives additional information and clearly understanding of the main idea of this paper. Otherwise, this paper review still not enough for comprehensive reviews and only considered as mini review due to the less contents and figures.

We believe that we have fully answered both comments 1 and 3 and trust that the reviewer considers the paper suitable as a full review.

Reviewer #5: The revised manuscript has addressed most of my comments and adopted most of my suggestions. By explicitly describing and summarizing the previous findings, the manuscript has substantially improved after the revision. There are some amendments needed.

1. The formats of table and graphs are not regular. For example, the font used in the table is not uniform in Table3 (Page11). And there lacks consistent format in one graph (including the font size, format, graph size). Other than that, the formats of the whole manuscript should be checked.

The font size throughout the paper has been checked especially for Table 3.

2. please check and correct the errors in the table (Page16, Line 11 and 34-35 2g LA).

The errors have been corrected in Table 4 pages 21-22

3. Scheme 3 uses the image of the referenced paper directly, which is not

recommended. Therefore, the authors are suggested to draw their own mechanism diagrams.

Scheme 3 has been redrawn.