Review

Heterogeneous Catalyzed Biodiesel Production Using Cosolvent: A Mini Review

Haris Mahmood Khan 1,*, Tanveer Iqbal 1, Saima Yasin 2, Muhammad Irfan 3, Muhammad Mujtaba Abbas 3,*, Ibham Veza 4, Manzoore Elahi M. Soudagar 5,6, Anas Abdelrahman 7 and Md. Abul Kalam 8

1 Department of Chemical, Polymer and Composite Materials Engineering, University of Engineering and Technology (New Campus), Lahore 54890, Pakistan; tanveer@uet.edu.pk (T.I.); m.irfan@uet.edu.pk (M.I.)
2 Department of Chemical Engineering, University of Engineering and Technology, Lahore 54890, Pakistan; drsaima@uet.edu.pk
3 Department of Mechanical Engineering, University of Engineering and Technology (New Campus), Lahore 54890, Pakistan
4 Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, Durian Tunggal 76100, Melaka, Malaysia; ibhamveza@utem.edu.my
5 Department of Mechanical Engineering and University Centre for Research & Development, Chandigarh University, Mohali 140413, Punjab, India; me.soudagar@gmail.com
6 Department of Mechanical Engineering, School of Technology, Glocal University, Delhi-Yamunotri Marg, SH-57, Mirzapur Pole 247121, Uttar Pradesh, India
7 Department of Mechanical Engineering, Faculty of Engineering & Technology, Future University in Egypt, New Cairo 11845, Egypt; anas.mohamed@fue.edu.eg
8 Department of Engineering and IT, University of Technology Sydney, Ultimo, NSW 2007, Australia; mdabul.kalam@uts.edu.au

* Correspondence: hariskhan@uet.edu.pk (H. M. K.); m.mujtaba@uet.edu.pk (M. M. A.)

Abstract: Biodiesel is gaining recognition as a good replacement for typical diesel owing to its renewable, sustainability, and eco-friendly nature. Transesterification is the leading route for biodiesel generation, which occurs during homogeneous/heterogeneous/enzymatic catalysis. Besides this, the usage of heterogeneous catalysts is considered more advantageous over homogeneous catalysts due to the easy catalyst recovery. Consequently, numerous heterogeneous catalysts have been synthesized from multiple sources with the intention of making the manufacturing process more efficient and cost-effective. Alongside this, numerous researchers have attempted to improve the biodiesel yield using heterogeneous catalysts by introducing cosolvents, such that phase limitation between oil and alcohol can be minimized. This short review is aimed at examining the investigations performed to date on heterogeneously catalyzed biodiesel generation in the presence of different cosolvents. It encompasses the techniques for heterogeneous catalyst synthesis, reported in the literature available for heterogeneous catalyzed biodiesel generation using cosolvents and their effects. It also suggests that the application of cosolvent in heterogeneously catalyzed three-phase systems substantially reduces the mass transfer limitation between alcohol and oil phases, which leads to enhancements in biodiesel yield along with reductions in values of optimized parameters, with catalyst weight ranges from 1 to 15 wt. %, and alcohol/oil ratio ranges from 5.5 to 20. The reaction time for getting the maximum conversion ranges from 10 to 600 min in the presence of different cosolvents. Alongside this, most of the time, the biodiesel yield remained above 90% in the presence of cosolvents.

Keywords: heterogeneous catalyst; transesterification; cosolvent; biodiesel; yield

1. Introduction

In the present era, most research has been concentrated on addressing the current energy crisis, while keeping environmental protocols and global climate change as the
priority. The drastic reduction in fossil fuel reserves and growing ecological issues have instigated the exploration of alternate energy supplies in order to justify the rising energy challenges of the world, along with achieving the target of controlled emissions. Therefore, renewable and ecofriendly fuels are required to be introduced into current energy systems. Biofuels, including biodiesel and bioethanol, are thought to be renewable fuels, and a good substitute of mineral diesel and gasoline, respectively. Moreover, their quick production with resource conservation and minimal energy requirements is also equally crucial [1–3]. Animal fats and vegetable oils are used as feedstocks to yield biodiesel, and therefore, biodiesel is believed to be a renewable fuel as it originates from bioresources. Biodiesel is a biodegradable, non-toxic and ecofriendly fuel, as its combustion generates fewer emission, pollutants and carcinogens [4,5]. The usage of biodiesel in a typical diesel fuel engine does not require any alternation, owing to its analogous characteristics to those of mineral diesel, thus making it a good replacement for diesel fuel [6].

The most prominent technique utilized for biodiesel generation is called transesterification/alcoholysis, in which one type of ester is transformed into another type [7–9]. In transesterification, the usage of homogeneous, heterogeneous, or enzymatic catalysts speeds up the reaction [10–14]. The application of homogeneous catalysts in transesterification yields good catalytic activity, but the catalyst recovery is difficult in cases of homogeneous catalysts, and requires additional washing stages; therefore, the overall production process becomes cost-intensive [15]. This problem could be resolved by the application of heterogeneous catalysts [16]. Several heterogeneous catalysts have been developed by researchers to transform triglycerides into biodiesel [17–21]. The in situ preparation of Ca–Mg–Al hydrotalcite on ceramic membranes was also examined to produce biodiesel [22]. Some researchers have studied the kinetic modeling and thermodynamics of biodiesel generation in the presence of heterogeneous catalysts [23,24]. Although efficient heterogeneous catalysts have been manufactured to convert oil into biodiesel through transesterification reactions, mass transfer limitations between three-phase mixtures may limit the reaction speed that would otherwise be achieved in the absence of these limitations [25]. For instance, vegetable oil and methanol are immiscible and appear in two phases. Due to the presence of phase interface, less mass transfer can occur. Numerous techniques have been discussed in the literature to avoid this restriction. One solution is the application of a suitable pacing style to blend these two phases. Increases in temperature may be another solution, but this makes the process more energy intensive. Furthermore, the boiling point of methanol may limit the choice of temperature increases. Several researchers have demonstrated the usage of cosolvent to make methanol and oil soluble into each other, with considerable enhancements in reaction rate [26–32]. Both polar and non-polar sites of cosolvents assist oil and methanol phases, with diminishing surface tension, and therefore create a single phase in the reaction, which can proceed under mild conditions with shorter reaction times. It has been reported several times that the application of the cosolvent technique may lessen the reaction temperature and reaction time, and enhance the fuel properties of biodiesel [33–35]. Therefore, it has become essential to adopt efficient and resource-conservative processes with minimal costs to satisfy the rising demands for fuels.

This short review is aimed at reviewing the investigations performed to date on solid catalyzed biodiesel generation in the presence of different cosolvents. It encompasses the techniques for heterogeneous catalyst synthesis, reported in the literature available on heterogeneous catalyzed biodiesel generation using cosolvents and their effects. It also suggests that the application of cosolvents in heterogeneous catalyzed three-phase systems substantially reduces the mass transfer limitation between alcohol and oil phases, which leads to enhancements in biodiesel yield along with reductions in the values of optimized parameters.

2. Techniques for Heterogeneous Catalyst Synthesis
There are several techniques available in the literature for the synthesis of heterogeneous catalysts, including wet impregnation, calcination, co-precipitation, the sol-gel method, calcination–hydration–dehydration, physical mixing, bi-functional modification, etc., and these techniques are indicated in Figure 1 [7,36–42]. The heterogeneous catalysts can be made from chemicals, or may be synthesized from waste-based resources, such as agricultural waste, bones and eggshells [19,36,43]. Metal and mixed metal oxide-based heterogeneous catalysts, such as oxides of Ca, Mg, Sr, calcium methoxide, sulfated zirconia and aluminum oxide-based catalysts, are commercially available, and others can be synthesized from different sources using different techniques [44–47]. At the same time, it has become necessary to adopt environmentally benign methods of catalyst preparation, so that the commercial-scale production of catalysts can be practically feasible and environmentally protective. Therefore, nowadays, most heterogeneous catalysts have been developed from waste-based and biomass resources using ecofriendly techniques [48–51].

3. Heterogeneous Catalyzed Biodiesel Generation Using Cosolvents

The transesterification reaction involves methanol and oil in the existence of a catalyst (homogeneous/heterogeneous/enzymatic). When using heterogeneous catalysts in a biodiesel synthesis reaction, a three-phase system (oil/alcohol/catalyst) evolves in the reaction mix. In general, the reaction rate in the occurrence of a heterogeneous catalyst is slower than when using a homogeneous catalyst, owing to the mass transfer restriction. The usage of cosolvents, including tetrahydrofuran (THF), dimethylether (DME), etc., in the existence of homogeneous catalysts such as KOH significantly increases the rate of reaction, which might be due to the exclusion of mass transfer resistance between the oil and methanol layers. The joint solubility of methanol and oil could be enhanced at lower reaction temperatures by using cosolvents, and therefore, the reaction rate may increase,

Figure 1. Catalyst synthesis methods for biodiesel generation [7].
and the materials can be recovered and reutilized easily [52]. It has been reported that butanolysis reactions proceed more quickly than methanolysis at the start of reaction, which may be because of the good miscibility of butanol and oil, thus lowering the inter-phase mass transfer resistance [53]. In the occurrence of diethylether as the cosolvent, the reaction was accelerated 100 times, and finished in 10 min when using acetone as the cosolvent in the existence of potassium hydroxide as the catalyst; this may be due to the vanishing of mass transfer resistance between phases [54]. Moreover, a number of cosolvents, such as acetone, tetrahydrofuran, iso-propanol, n-hexane, toluene, di-isopropyl ether, acetonitrile, petroleum ether, xylene, ethyl acetate, glymes and biodiesel itself, have been employed to reduce phase resistances, as described in Table 1. Therefore, researchers have begun to probe the effects of cosolvents on biodiesel yield when using heterogeneous catalysts, as indicated in Table 1.

Laskar et al., 2020 [31] reported on biodiesel generation using snail shell-derived heterogeneous catalysts, while employing acetone as the cosolvent. As per their studies, a 98% biodiesel yield was achieved at ambient temperature, within the short reaction time of 2 h, with the addition of 20 wt. % acetone. They established that the application of a cosolvent in the transesterification reaction raised the homogeneity between the phases, which led to higher biodiesel yields. In another study, the use of a calcium aluminum oxide (Ca₂Al₂O₅) as the heterogeneous catalyst, made by the solid-state method, was assessed for biodiesel generation from waste vegetable oil using acetone as the cosolvent. More than 97% biodiesel yield was achieved within 25 min, using 20 wt. % of acetone as the cosolvent and keeping the methanol to oil ratio at 6/1 [55]. They concluded that the application of a cosolvent considerably lowers methanol consumption and reaction time as compared to other traditional approaches.

In another investigation, Sahani et al. [56] reported on biodiesel generation using a strontium lanthanum mixed metal oxide catalyst in the occurrence of di-isopropyl ether (DPE) as the cosolvent. They concluded that more than 96% conversion was obtained within 40 min, at a catalyst weight of 1.5 wt. %, while using DPE as the cosolvent. The greater conversion may have resulted owing to the capacity of the cosolvent to enhance the stability of the polar methanol in the mixture through hydrogen bonding, along with the alkyl group, which caught up the oil phase and acted as a carrier of methanol into oil as the phase transfer moiety.

Similarly, in another work, modified ZrO₂ was utilized as a solid catalyst in the transesterification of palm fatty acid distillate using toluene as a cosolvent. More than 90% biodiesel yield was obtained, keeping M/O at 9/1, catalyst loading at 0.5 wt. %, the reaction time at 120 min, the reaction temperature at 80 °C and the toluene at 10% v/v. The usage of toluene as cosolvent resulted in a yield enhancement at lower alcohol to oil ratios, keeping the biodiesel yield above 90% [57].

Madhu et al. [58] reported on biodiesel generation from Karanja oil using β-Tricalcium phosphate (β-Ca₃(PO₄)₂) as the solid catalyst in the presence of tetrahydrofuran (THF) as the cosolvent. In their study, a 97% biodiesel yield was accomplished within 90 min at the catalyst weight of 2.5 wt. %, while using THF as a cosolvent. They concluded that using the THF as a cosolvent achieved the highest biodiesel yield, as it facilitated the conversion of the two-phase system into one phase. Similarly, at elsewhere, Sr–Al double oxides were used as the heterogeneous catalysts to transform lard oil into methyl esters in the occurrence of tetrahydrofuran as the cosolvent. More than 99% biodiesel yield was obtained at a catalyst loading of 0.9 wt. % within 45 min, using THF as the cosolvent and keeping methanol to oil ratio at 5.5/1 [26].

Similarly, in another investigation, calcium-based catalysts derived from scallop shells were utilized as the heterogeneous catalysts for the transformation of a mixture of oils into biodiesel using acetone as cosolvent [27]. More than 85% biodiesel yield was gained at the catalyst weight of 5 wt. %, using the cosolvent of Vsolvent/Vmethanol = 0.36. In another study, an OH-impregnated heterogeneous catalyst was successfully utilized in the transformation of refined coconut oil into biodiesel, using tetrahydrofuran as the
cosolvent [59]. The highest conversion rate of 81.70% was realized using this cosolvent (0.58 mol% of oil) in a 10 min reaction time. Some researchers used supercritical CO2 and cosolvents to effectively extract oil from seeds, which was later converted into biodiesel [60]. Some other researchers also used cosolvents in the presence of heterogeneous catalysts, and converted oil into biodiesel with the help of ultrasound energy [61,62]. The usage of non-conventional techniques involving microwave energy, ultrasound energy and plasma heating makes the biodiesel generation process more efficient.

The above-mentioned studies indicate that the presence of a cosolvent in heterogeneously catalyzed biodiesel generation significantly reduces the phase resistance, which leads to higher yields of biodiesel along with reductions in the values of other optimized parameters, including alcohol/oil ratio and reaction times. Furthermore, a review has recently been published on the usage of deep eutectic solvents in the manufacturing of biodiesel [63]. Different types of deep eutectic solvents have been found useful in the esterification of free fatty acids [64–66].

Table 1. Summary of recent works reported for heterogeneous catalyzed biodiesel generation using various cosolvents.

| Catalyst | Catalyst preparation | Feedstock | Cosolvent | Reaction parameters (MeOH/O, Catalyst wt. %, Time, Temperature, Cosolvent) | Yield | References |
|----------|---------------------|-----------|-----------|-------------------------------------------------|--|------------|
| CaO as heterogeneous catalyst | The catalyst was synthesized from waste snail shells via calcination for the specific time and temperature. | Soybean oil | Acetone | 6, 3, 120, 28, 20 wt. % of oil | Y = 98 | [31] |
| River snail shells-derived CaO | The biomaterial was scrubbed with water and dried followed by grinding, sieving and calcination at various temperatures (600–1000 °C) for 3 h. | Palm oil | Tetrahydrofuran (THF) | 12, 5, 90, 65, 10% v/v (THF in methanol) | Y = 98.5 ± 1.5 | [67] |
| Scalable imidazolium salts-based solid acid | 1,3-disulfonic acid imidazolium chloride and anhydrous ferric chloride were used to prepare the 1,3-disulfonic acid imidazolium tetrachloroferrate. | Firmiana platanifolia oil | Biomass-derived tetrahydrofuran (THF) | 15, 5, 480, 120, 48.8 mmol THF | Y = 97 | [68] |
| Calcium aluminium oxide catalyst | Solid state technique was applied for the synthesis of calcium aluminium oxide using CaCO3 and Al2O3 calcined at 900 °C. | Waste vegetable oil | Acetone | 6, 1.2, 25, 55, 20 wt. % of acetone | C = 97.98 | [55] |
| OH-impregnated CaO as heterogeneous catalyst | OH-impregnated CaO was synthesized by wet impregnation method | Refined coconut oil | Tetrahydrofuran (THF) | 6, 5, 10, 60, 0.58 mol% of oil | C = 81.70 | [59] |
| Strontium lanthanum mixed metal oxide | Co-precipitation method was used to prepare strontium lanthanum mixed metal oxide | Schleichera oleosa oil | Diisopropyl ether (DPE) | 14, 1.5, 40, 60, cosolvent to alcohol molar ratio, 1/1 | C = 96.37 | [56] |
| Catalyst Description | Synthesis Methodology | Product | Amount | Yield (%) | Reference |
|----------------------|-----------------------|---------|--------|-----------|-----------|
| SO₄²⁻/SnO₂–SiO₂ (solid acid catalyst) | Sulfated tin oxide carried with silica was synthesized as per method reported by Lam et al. [30] | Waste cooking oil | 15, 6, 90, 150, biodiesel as cosolvent | Y = 88.2 | [69] |
| Na/NaOH/-Al₂O₃ heterogeneous base catalyst | The successive processing of γ-Al₂O₃ with sodium hydroxide and sodium at 320 °C under nitrogen was carried out to prepare the Na/NaOH/-Al₂O₃ catalyst accompanied by the technique suggested by Suzukamo et al. [70]. | Soybean oil | 9, 1g, 120, 60, 5:1 (oil to n-hexane molar ratio) | Y = 94 | [71] |
| Mg–Fe mixed oxides | Hydrotalcite was used to prepare Mg–Fe mixed oxides through calcination for 3 h | Rapeseed oil | 24, 1, 240, 120, methanol and butanol at a molar ratio of 1/1 | C = 97.5 | [29] |
| Limescale (kettle limescale deposit) | The catalyst was synthesized from kettle limescale deposit after crushing, grinding and sieving followed by oven drying. Subsequently, the catalyst was calcined at 900 °C. | Waste cooking oil | 2.15/5 (v/v), 7.875, 12.5, 60, acetone concentration (pure oil-based) of 13.95 wt. % | C = 97.16 | [72] |
| Calcium oxide (CaO) derived from eggshell | The eggshell material was heat-treated at designated temperature of 800 °C in air for 3 h to generate CaO materials | Palm oil | 12, 13, 600, 75 ±2, 10% v/v of acetone | Y = 97.5 | [73] |
| Mg–Al hydrotalcites | Hydrotralcites were synthesized by the cosolvent method | Canola oil. | 6, 3, 540, 60, cosolvent content: 10 wt. % | C > 60 | [74] |
| SrO doped SiO₂ (SrO/SiO₂) | The sol–gel approach was applied to prepare SrO-doped CaO and SrO-doped SiO₂ catalysts | Refined olive oil | 6, 5, 30, 45, hexane to olive oil (volume basis)/1/2 | Y > 90 | [75] |
| Novel catalyst (β-tricalcium phosphate) | The catalyst was produced by the calcination of ground fish bones at various temperatures, ranging from 600 °C to 900 °C for 4 h | Karanja oil | 10, 2.5, 90, 65, (THF): methanol 1:1 | Y = 97 | [58] |
| Calcium-based catalysts | The scallop shells were calcined at 800 °C for 3 h to derive Ca-based catalysts | Mixture of 50 wt. % (soybean oil and non-edible beef tallow) | 12, 5, 150, 65, (Vsolvent/V methanol=0.36) | Y = 85.3 | [27] |
| Modified ZrO₂ | WO₃–ZrO₂ was produced through incipient wetness impregnation of sulfuric acid or ammonium meta tungstate over zirconium oxide (ZrO₂), prepared via the precipitation technique | Palm fatty acid distillate (PFAD) | 9, 0.5, 120, 80, 10% v/v | Y > 90 | [57] |
| **CaO** | Calcined at 700 °C for 5 h and stored in oven. | Rapeseed oil | Tetrahydrofuran (THF) | 12, 2.5, 360, 60, THF (30.0 wt. %) Y >90.0 | 76 |
|---|---|---|---|---|---|
| **Calcium methoxide catalyst** | The calcined quick lime powder was utilized to prepare calcium methoxide by reacting it with methanol at a specific temperature for 2 h | Waste cooking oil | Tetrahydrofuran (THF) | 11.6, 2.83, 100.14, 65, 8.65% v/v of THF in methanol concentration | 77 |
| **Sr−Al double oxides** | The sol-gel citrate method was applied to prepare Sr−Al mixed oxides | Lard oil | Tetrahydrofuran (THF) | 5.5, 0.9, 45, 50, 5 wt. % THF Y = 99.7 | 26 |
| **Quaternized polysulfone alkali-catalyzed membrane** | The solvent evaporation phase inversion method was employed to synthesize a series of alkaliized polysulfones APSF membrane. | Soybean oil | n-hexane | 10 g soybean oil/10 g methanol, 25 wt. % of soybean oil mass, 240, 60, 50 wt. % hexane as cosolvent | 78 |
| **Calcium methoxide** | The quick lime was employed to make calcium methoxide catalyst | Palm stearin | Tetrahydrofuran (THF) | 9.39, 2.33, 102, 65, 9.07% v/v based on methanol of THF cosolvent C = 98.23 | 79 |
| **Eggshell-derived catalyst** | Calcined at 850 °C for 3 h | Jatropha oil | Acetone | 9, 7, 120, 65, 1:1 (acetone/oil) weight ratio Y = 93 | 80 |
| **TiO2-supported ZnO catalyst** | The catalyst was manufactured by the impregnation of titanium support with zinc nitrate accompanied by drying and calcination | WCO | Hexane | 18, 10, 60, 200, hexane to oil mole ratio of 1/1 C > 90 | 28 |
| **Zeolite Y interchanged with CsCl** | The zeolites Y411 and Y756 were treated with CsCl using 1M and 0.5M solutions. | Waste vegetable oil | Tetrahydrofuran (THF) | 80, 2.5, 270, 65, 10 wt. % concentration of cosolvent Conversion increase = 9 to 18% | 81 |
| **CaO/scoria (a kind of ignition rock)** | The wet impregnation technique and calcination were applied to prepare the catalyst | Waste cooking oil | n-hexane | 14.76, 12, 262, 59.7, n-hexane to oil volume ratio = 0.905/1 C =97.7 | 32 |
| **CaO** | Anhydrous calcium oxide (99.99% purity) was procured | Soybean oil | Glymes | 430 μl/700μl, 0.03g, 240, 60, 300 μl glyme C = 99 | 82 |
| **CaO as heterogeneous catalyst** | The CaO catalyst was procured and activated using methanol | Soybean oil | Iso-propanol | 20, 30 mg, 6.5, 65, 14.5 wt. % Y = 99 | 83 |
| **CaO catalyst was procured and used** | CaO catalyst was procured and used | Linseed oil | Diethyl ether (DEE) | 9.48, 160 g CaO, 180, 30, DEE/methanol ratio of 1.19:1 (continuous mode) Y = 98.08 | 84 |
| **Carbon based heterogeneous catalyst** | The catalyst was synthesized using hydrothermal carbonization, sulfonation and combination of two. | Palm fatty acid distillate (PFAD) | Tetrahydrofuran (THF) | 6, 3, 180, 333K, THF: 0.2% of PFAD feedstock, ultrasonic assisted 120W C = 86 | 61 |
| **Calcined sodium silicate as heterogeneous catalyst** | The sodium silicate was purchased, dehydrated and calcined in furnace | Refined soybean oil | Petrodiesel | 9, 3, 120, - , 10 wt. % of cosolvent, ultrasonic assisted 20 KHz Y = 97 | 62 |
4. Optimization of Reaction Parameters for Heterogeneously Catalyzed Biodiesel Generation Using Cosolvents

In order to attain the maximum biodiesel yield from the heterogeneously catalyzed system using cosolvents, the optimization of reaction parameters, such as the ratio of alcohol to triglyceride, the reaction temperature, the catalyst loading, the reaction time and the amount of cosolvent, is required. For instance, Table 1 indicates the optimized values of reaction parameters whereby maximum biodiesel can be attained in the existence of cosolvents while using heterogeneous catalysts. Different cosolvents, such as acetone, tetrahydrofuran, iso-propanol, n-hexane, toluene, di-isopropyl ether, glymes and biodiesel itself, have been employed in specified quantities to obtain the maximum yield of biodiesel [56,59,67,69,71,82]. For instance, in the case of river snail shells-derived heterogeneous catalysts, the reaction time was significantly reduced from 180 min in a non-cosolvent reaction to 90 min in a cosolvent reaction with 10% v/v THF [67]. Similarly, it has been reported that the usage of calcium aluminum oxide as a heterogeneous catalyst using cosolvent substantially reduces the reaction time and methanol consumption in comparison with conventional methods [55]. In another investigation, a significant reduction in reaction time was reported using eggshells-derived heterogeneous catalysts along with acetone as cosolvent, with a biodiesel yield of 93% [80]. Since the application of cosolvents substantially reduces the phase resistance, numerous investigators have claimed reductions in optimized parameters, such as alcohol to oil ratio and reaction time, in the presence of cosolvents. In another study, different cosolvents such as propane, heptane, CO₂, n-hexane, dimethyl ether, toluene, cyclohexane and ether have been utilized for the conversion of coconut oil into biodiesel using supercritical methanol [85]. Ether was found to be the best cosolvent with respect to biodiesel yield. Nowadays, different software such as mini tab, RSM, ANN, etc., are being utilized in experimental designs for the optimization of reaction parameters.

5. Conclusions

Nowadays, some investigations are being carried out to make the biodiesel generation process more efficient using cosolvents in the presence of heterogeneous catalysts to minimize the phase resistances between alcohol and oil. It has become essential to adopt efficient and resource-conservative processes, with minimal costs, in order to satisfy the rising demands for fuels. This short review is aimed at examining the investigations carried out to date on solid catalyzed biodiesel generation in the presence of different cosolvents. It encompasses the techniques for heterogeneous catalyst synthesis, reported in the literature available on heterogeneous catalyzed biodiesel generation using cosolvents and their effects. It concludes that the application of cosolvent in heterogeneous catalyzed three-phase systems substantially reduces the mass transfer limitation between alcohol and oil phases, which leads to enhancements in biodiesel yield along with reductions in the values of optimized parameters such as reaction time, reaction temperature, methanol consumption and catalyst amount. The reaction time for deriving the maximum conversion ranges from 10 to 600 min in the presence of different cosolvents. Additionally, most of the time, the biodiesel yield stayed above 90% in the presence of cosolvents. A variety of cosolvents, such as acetone, tetrahydrofuran, iso-propanol, n-hexane, toluene, di-isopropyl ether, glymes and biodiesel itself, can be employed in specified quantities to obtain the maximum yield of biodiesel. Different researchers found that different cosolvents were appropriate to their specific studies, and the degree of appropriateness was directly associated with economics, biodiesel yield and separation properties. Thorough investigations related to the ecological aspects of different cosolvents are yet to be carried out.

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