Catalysts for Transesterification

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1 Introduction

Chemically, biodiesel is monoalkyl esters of long chain fatty acids derived from renewable feed stock of vegetable oils and animal fats. This has been proposed as an engine fuel by Rudolf Diesel about 100 years ago. Biodiesel is produced by transesterification in which oil or fat is reacted with a monohydric alcohol in the presence of a catalyst. The transesterification reaction usually dependent on a number of parameters, particularly on the molar ratio of alcohol to oil, type and amount of the catalyst, reaction time and temperature and purity of the reactants. In this presentation we shall restrict only to the catalysts since the choice of catalyst is the first step for designing an appropriate transesterification system and out line the considerations that go in the selection of catalysts for this particular reaction. The chosen catalyst system can be homogeneous, or heterogeneous or enzymatic type.It is therefore natural that depending on the type of catalyst system chosen the resultant process parameters especially the molar ratio of oil to alcohol and temperature have to be optimized. There have been consistent considerations in literature for evaluating the various possible catalysts that can promote the reaction as short time as possible and also can sustain other adverse experimental conditions like aqueous medium, abnormal oil to alcohol ratio.

2 Catalysts

2.1 Homogeneous Catalysis

2.1.1 Acid Catalysis

This type of catalysis is preferred and better suited when the oil contains higher fatty acid (high free fatty acid (FFA) content feedstock like waste vegetable oil which can be converted to biodiesel [1]) [?] and moisture. The typical catalysts include sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acids. Acid catalyzed transesterification yields in alkylesters but suffers from a slow reaction rate, thus leading to longer reaction times and some times high temperature is also required to give complete conversion. For example, the common acid catalyst employed is sulfuric acid which requires more than 50 hours to yield complete conversion of soyanbean oil with methanol to oil ratio of 30:1 at 338 K. Since the reaction is very sluggish reaction rate the reaction parameters employed are more drastic like methanol/oil ratio (20-300:1) high acid content (low pH) and reaction temperatures in the range of 423-523 K.Another disadvantage of acid catalyzed reaction is that the simultaneous side reaction of formation of carboxylic acid thus necessitating to carry out the reaction in the absence of water.

2.1.2 Base Catalysis

The common base catalysts employed are alkaline metal hydroxides (NaOH and KOH mostly) and alkaline earth metal hydroxides and alkoxides. The factor in favour homogeneous base catalysis for transesterification is high conversion levels in short reaction times. However, there are major drawbacks like energy intensive, difficulty in the recovery of glycerol and the catalyst from the reaction mixture. There are distinct limitations in homogeneous catalysis for transesterification, They are:
(1) These processes require elaborate downstream treatment involving variety of unit operations like neutralisation and drying.
(2) The catalysts cannot be easily separated from the reaction mixture as they dissolve in the glycerol layer and also partially in biodiesel.
(3) Separation procedures are expensive involving energy intensive distillation.
(4) Catalysis by alkaline metal hydroxides can be affected by water arising either as a reagent impurity or through the reaction of hydroxide and methanol.
(5) One of the main drawback of this process is the corrosion of the reactor and pipelines by dissolved acids/base species thus inevitably increasing the material cost for process construction.
(6) Homogeneously catalyzed transesterification is not amenable for continuous processing.
In order to overcome some of these limitations, attempts have been made to use non-ionic organic bases as catalysts. It therefore appears that homogeneous catalysis may not be appropriate for economical and commercial adaptation of transesterification.

3 Enzyme catalysis

Generally enzymes, lipases promote the transesterification in both aqueous and non-aqueous medium. Enzymatic processing has the added advantage of elimination of the down stream processing for product purification. This is so because the by-product glycerol can be easily removed with out any complex unit operations and also the free fatty acids contained in waste oils and fats can be completely converted to alkyl esters. However it should be kept in mind that the production cost of lipase or enzyme catalysts can be significantly greater than that of other catalyst systems.

4 Heterogeneous Catalysis

There are specific advantages in adapting to heterogeneous catalysts for transesterification. These include:
(1) These systems are non-coorosive with no undesired environmental effects

Table 1: Types of heterogeneous base catalysts proposed for transesterification[2]

simple one component metal oxides	alkali metal oxides alkaline earth oxides rare earth oxides Thoria, zirconia, zinc oxide and titania
Zeolites	Alkali ion exchanged zeolite alkali ion supported zeolite
Supported alkali or alkaline earth metal	Alkali metal ions on alumina or silica Alkali metal on alkaline earth oxides Alkali metals and alkali metal hydroxides on alumina
Clay minerals	Hydrotalcites Crysotile Sepiolite
Non-oxides	Alkaline alkoxide Alkaline carbonate Guanidine-containing catalysts

(2) The constituents can be possibly easily separated and also recycled.
(3) The process is amenable for continuous operation.
(4) These catalyst systems are highly selective and their catalytic property depends on the surface properties which is amenable for modulation.
(5) Both acid and base functionality can be included in these solid catalysts and hence they can be used for oils with high fatty acids contents like waste coking oils. However, Heterogeneous processes have their own limitations.
(1) The heterogenously catalyzed process is slow as compared to the homogeneous catalyzed reactions and the intensification of reaction conditions (namely reaction temperature, methanol/oil ratio and catalyst amount) is a necessity for heterogeneous process.
(2) It is possible the active species (the leaching of the catalyst) may dissolve in the liquids and thus can affect the quality of the biodiesel produced and also cast shadow on the heterogenous nature of the reaction.
(3) There can be deactivation of the catalyst surface by the adsorption of acidic hydrocarbons on the basic sites thus necessitaing the regeneration the catalyst from cycle to cycle.
Although solid acid catalysts are well known in the literature, a variety of solid base catalysts have been proposed for transesterification. one simple compilation is given in Table 1. Solid basic catalysts have not been so much recognized as the counter part solid acid catalysts even though one could have considered this possibility on the basis of complimentary nature. This situation could have been due to the fact that the basic sites are easily occupied with atmospheric components like CO_2, H_2O and O_2 that can generate carbonate, hydroxide and peroxide respectively and incapacitate the function of the basic sites. However, it was recognized in 1970 that the basic sites could be resurfaced with appropriate thermal treatment (>750 K) which could re-evolve the covered substrates. In general, solid base catalysts have been receiving attention for many industrial hydrocarbon conversion reactions [3]. There are also some seminal publications in the literature on the use of base catalysts like

Table 2: The experimental data showing the relationship of basicity with biodiesel production yield[2,5]

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Serial number	catalyst system	percentage biodiesel production
1	γ - Alumina	4
2	Na/Al_2O_3	74
3	$NaOH/Al_2O_3$	62
4	$Na/NaOH/Al_2O_3$	82

Table 3: Typical data on the transeseterification on CaO Catalyst

methanol to oil ratio	wt% of CaO	Temp K	time (min)	% yield	ref
12:1	8	338	90	95	6
6:1	3	338	60	96.6	7
9:1	1.5	343	150	93	8
12:1	1.5	343	120	95	9

$Na/NaOH/Al_2O_3$ for base-catalyzed transesterification for biodiesel synthesis [4]. These studies have revealed some of the important facts like the super basicity of the $Na/NaOH/Al_2O_3$ system. The intrinsic basic character of this catalyst system has been probed by X-ray photo-electron spectroscopy wherein it has been observed that the binding energy of 1s electron of surface oxygen is shifted to lower values with respect to that of oxygen in pure alumina indicating the electron donating ability is sufficiently altered when alumina is modified with Na and NaOH. The data given in Table 2 demonstrates that the strength of the basicity of the solid catalysts has a direct relationship on the yield of biodiesel production.

4.1 Single Component Metal Oxide Catalysts

Alkaline earth oxides like SrO, BaO can adsorb oxygen to form peroxide type species and they need to be activated thermally to reveal the basic oxide sites for transesterification.[10]. Cao is one of the basic catalysts that has been extensively studied for transesterification reaction. The interesting feature of this catalyst system is the water tolerance, since in most of the catalyst systems, the presence of water will have adverse effect on the yield of Fatty acid methyl esters (FAME). Some typical data on the transesterification of oil on CaO catalyst are assembled in Table 3. However under microwave conditions, it has been observed that the amount of methanol required is reduced in addition to the reaction time. Various other oxides have been employed as catalysts for transesterification, these include: PbO, MnO_2, Tl_2O_3, Pb_3O_4, Li or Na or K or Mg or Ca/ZrO_2.

4.2 Zeolites as Transesterification Catalysts

NaX zeolite when loaded with 10% KOH showed considerable activity for the transesterification of soybean oil with methanol in the ratio of 1:10 with 3 wt% of the catalyst gave 85.6% yield in 8 h.[10]. A Variety of other zeolite based systems have been employed successfully for transesterification of various oils

Table 4: Data on transesterification on zeolites

Oil type	catalyst system	conversion %	Ref
Soybean oil	Mg-MCM 41		11
	Mg-Al Hydrocalcite	97	
	K impregnated Zirconia		
	Modified Zeolite Y	98.4	12
	Natural clinophlolite	86.9	12
sunflower oil	NaX/CaO	93.5	13

like Jatropha curcas, sunflower oil,vegetable oils and soybean oil. The relevant data are briefly summarized in Table 4. Various comparisons have been made on the activity of the substituted or loaded zeolites with Cao, MgO and $Ba(OH)_2$ for the transesterification of vegetable oil and it has been shown that Li/CaO and $Ba(OH)_2$ showed highest activity among all the catalysts [14].

4.3 Supported Alkali/Alkaline Earth Metals

Alkali and alkaline earth metals and their carbonates, hydroxides, halides and nitrates supported on alumina or silica have been examined as catalysts for transesterification [15]. Alumina loaded with a variety of potassium salts like KI, KF,K_2CO_3 and KNO_3 (35% loading) have been examined for transesterification of canola oil and it has been shown that the system KF/Al_2O_3 showed highest activity and conversion. Similar results were obtained in the transesterification of Castor oil, palm oil and soybean oil and the reaction has also proved to be better under microwave irradiation. Superbasic catalyst was generated by loading sodium azide on gamma alumina and used for the soybean transesterification. In a recent study, mesoporous alumina and silica- supported (essentially Ca and K as active constituents)systems have been shown to give nearly 100% yield in transesterification reaction[16].

4.4 Clay Materials as Catalysts for transesterification

Hydrotalcites are layered double hydroxides with carbonate intercalation of the typical formula $Mg_6Al_2(CO_3)(OH)_6.4H_2O$ with anion exchange capacities. Hydrotalcites with Mg/Al ratio of 3 modified with Zn,Sn,Ba,Mn,Ce and Ca have been used for transesterification of soy oil and best results have been reported [17]. New catalyst system containing ferric ions substituted for aluminium ions with stronger base properties have been used for the tranesterification of triaetin and of soybean oil[18]. The activities of hydrotalcite, Cs-sepiolite and Cs-MCM-41 for transesterification of triglycerides showed that hydrotalcite showed nearly 92% conversion though the other two showed only 45 and 26% conversion only[19]. There are various studies reported in literature on the elucidating the optimum conditions for the use of hydrotalcite catalyst systems[20]. The perceptible basicity of systems generated from hydrotalcites (by thermal treatments) could have arisen due to the layer structure of the system and hence cation-anion distances could be such that the ionicity on oxygen is considerable which is considered to be a memory effect. However this postulate needs complete verification by XPS and other techniques.

4.5 Catalysts based on Non-oxides

Non metallic organic compounds mainly guanidine based systems namely Guanidine carbonate have been used as catalysts for the transesterification of vegetable oils upto 95% conversion. This process is already applied in an industrial pilot plant with a capacity of 1 ton/h [21]. A variety of polymer based catalysts has also been developed. Poly(hexamethylene biguanide (PHMBG) based network systems showed nearly full conversion though the kinetics of transesterification was 2 to 3 times slower as compared to the system based on uncross-linked PHMBG. Guanidinaes grafted to gel type polystyrene gave high conversions though the reaction kinetics is slow. To reduce the side reactions, biquanidines have been contained in polystyrene and thus showed that these catalyst systems can be recycled at least upto 10 cycles.[22].

5 Perspectives

Even though the research on transesterification has been maturing in the recent times. Though the conversion levels have reached the desired levels but it is necessary that the appropriate experimental conditions have to be established. Instead of looking for new catalyst systems it is necessary research efforts should be focused how the available catalyst systems can be exploited under favourable conditions like with lesser energy requirements (possibly low temperatures) without leachung of the catalyst under reaction conditions. It may be approprate if one can list out the possible perspectives for this reaction. (1) It is necessary that a continuous fixed bed process has to be realized for transesterification. (2) Correlations should be evolved between the cause and effect manner so that catalyst selection optimum operating conditions can be evaluated in a systematic manner and implemented. (3) The deactivation of the catalyst system and the recyclability of the catalyst system should be ensured. (4) Even though nearly 6 different type of catalyst systems have been established, it is necessary that focus is on a chosen system so that commercialization of the process is possible in the near future. (5) The future development process if it is to be heterogeneous, then the focus has to be reducing the temperature of operation, increasing the rate of the process, restricting the oil to methanol ratio, limiting the amount of catalyst to be used, establishing water tolerance and reducing the deactivation of the catalyst

6 References

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