PROGRESS ON POTENTIAL TECHNOLOGIES FOR GLYCEROL VALORIZATION INTO OXYGENATED FUEL ADDITIVES: A REVIEW

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Abstract

Glycerol has tremendous potential to be transformed into highvalue derivatives /functional chemicals. Demand for renewable sources, surplus availability, low cost and lower environmental impact have led to numerous selective processes for glycerol conversion into products for sustainability of bio-diesel industry. Bio-fuel derived platform molecules are in great demand as there is shift from petro-based chemicals to green chemicals and one of the main interests in the recent years is in the production of bio-fuel additives. This paper reviews different techniques and relevant catalysts used for the production of bio-fuel additives from different pathways such as esterification, etherification, acetalization and acetylation.

Keywords: *Crude Glycerol, Bio-diesel production, fuel additives, bioremediation, catalysts.*

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1. INTRODUCTION

Extensive use of petrochemicals have resulted in severe environmental crisis, depleting fossil fuels, escalating oil process, ever growing energy demands and poor health conditions (Yang et al. 2012, Trifoi et al. 2016). Hence emphasis has been given to alternate energy sources that respond to high energy demand and at the same time reduce use of fossil fuel resources and their relative impacts. Transesterification of triglyceride, a widely applied pathway for biodiesel production produces glycerol as a byproduct and contains impurities such as water, soap and fatty acids methyl esters (Luo et al. 2016). For every 100kg of biodiesel produced, 10 kg of bio glycerol is obtained as a byproduct (Ilham et al. 2016, Garlapati et al. 2016). The transformation of this byproduct facilitates the economy of the process and substantially enhances the economy of the biodiesel sector (Anitha et al. 2016).

Glycerol is a colorless, odorless, hygroscopic and viscous liquid that is sweet to taste (Sivasankaran et al. 2016). Also known by the name 1,2,3-Propanetriol or glycerin, it has a boiling point of 290^{o}C, melting point of 17.8^{o}C and a density of 1.261kgl^{-1}. Other specific characteristics of glycerol are mentioned in table:1. The three-OH (hydrophilic alcoholic hydroxyl group) explains the hygroscopicity of glycerol and its solubility in water, alcohol and insolubility in hydrocarbons (San Kong et al. 2016). Glycerol has diverse applications in different fields such as food, cosmetics, pharmaceuticals and polymer industries. It can also be transformed chemically and biologically to produce value – added chemicals such as hydrogen, ethanol, DHA, Propanediol, glycerol carbonate, acrolein, glyceric-acid, syngas, ethers, esters, etc (Papanikolaou et al, 2016, Bagheri et al, 2015).

Table 1: Physicochemical properties of glycerol(Ayoub et al. 2012)

Description	Values
Molecular formula Molar Mass	$C_3H_5(OH)_3$ 92.09g-mol^{-1}
Boiling Point (^{o}C)	290
Melting Point (^{o}C)	17.8
Flash Point (^{o}C)	160 (closed cup) 176(open cup)
Viscosity (Ps.S)	1.5
Density at 20^{o}C(g cm^{-3})	1.261
Heat of fusion at 18.07^{o}C (cal/g)	47.491
Auto ignition temperature (^{o}C) Critical temperature ^{o}C	400 492.2
Critical pressure (atm)	42.5
Dipole moment (30-50^{o}C)	2.68D
Dielectric Constant (25^{o}C)	44.38
Solubility in water Vapor pressure Refractive index	Miscible 0.003 mmHg (50^{o}C) 1.4746

The inherent problems that hinder widespread application of biodiesel is due to itspoor cold flow properties and dissimilarities with respect to viscosity, low-temperature flow, cold-filter plugging between methyl esters and petro-diesel. Also, when compared to biodiesel, gasoline and diesel as automotive fuels, biodiesel contributes less to fossil fuel depletion and climatic changes than the others, but was observed to cause more damage to the ecosystem with acidification, eutrophication and respiratory problems - caused by NO_xemissions (Asdrubali et al, 2015). Suggested solutions to these problems are to alter oil composition and winterization. One potential solution that may add benefit to biodiesel is the use of glycerol or its derivatives as fuel additives.

2. ACETALS AND KETALS

Glycerol acetalsare easy to synthesizeand can be used as additives for petroleum and alternative fuels and their blends. Glycerol ethers have known to reduce hazardous substances emitted during fuel combustion. Glycerol ethers of monohydric alcohols such as glycerol tert-butyl ethers reduced emissions of nitrogen-oxides, soot and carbon-monoxide and improve cold flow properties. Themain problems associated with ethers are their hydrophilicity. Mono ethers exibit miscibility with water and di-ethers are amphiphilic (Samoilov et al. 2016).Ketals are produced by the reaction of a ketone with analcohol in presence of a catalyst.Solketal- the acetone ketal of glycerol (2,2-Dimethyl -4-hydroxy methyl -1,3-dioxolane) is known to increase octane number of the fuel, reduces gum formation(Samoilov et al. 2016), decrease particulate emission, improve cold flow properties and improves oxidation stability. Solketal can be produced by catalytic reaction of glycerol with acetone in presence of catalyst (Figure-1). The low yield of solketal is due to the presence of water in the reaction. Water createsa kinetic and thermodynamic barrier and many researches tried solving this issuepresence.Different processes and catalysts have been developed

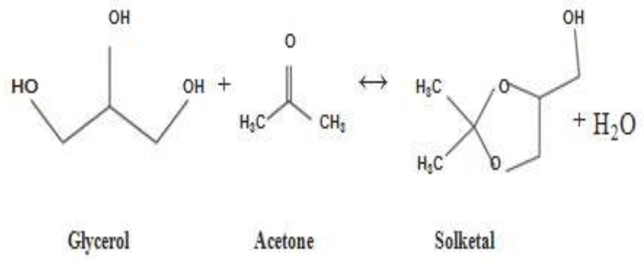


Fig 1: Conversion of glycerol to Solketal

Various catalysts have been employed to increase the conversion rate. Homogenous catalysts such as pTSA monohydrate.

The recoveries of catalysts in homogenous-chemical reactions areproblematic since they cannot be separated easily, besides corrode the reaction vessel and hence a disposal concern. To overcome these problems, heterogeneous catalysts can be employed such as silica induced heteropoly-acids – SiW(tungsto-silisic acid), PW(tungsto- phosphoric acid), PMo(molybdo-phosphoric acid), SiMo (molybdo-silisic acid)etc,. The reported glycerol conversion is more than 97% with selectivity of 99% towards solketal (Nanda et al, 2016). Amberlyst, zeolites, mont-morillonite, nafion are alsoextensively used in batch and continuous processes to enable better heat and mass transfer efficiency, easy scale-up with more economical and environmental benefits.

3. ACETYLATION OF BIO-GLYCEROL/ ESTERIFICATION OF GLYCEROL

Acetylation of bio-glycerol with acetic acid produces di and triacetin that has potential to be used as bio-diesel and petro-fuel additives. They are known to lower viscosity, meets flash point specification and oxygen stability. Also known as esterification, any reaction between glycerol and a poly carboxylic acid are known to produce mono, di and tri-acylglycerols also known as triglycerol ester. The reaction of acetic acid with glycerol produces monoacetin (2-monoacetyl -1, 3-propanediol or 3-monoacetyl -1, 2-propnediol, MAG) diacetin (1,2-diacetyl -3-propanol or 1,3-diacetyl propanol, DAG) and triacetin (1,2,3-triacetooxypropane or 1,3-Diacetyloxypropane-2-yl acetate, TAG). The reaction is as shown below

Glycerol + acetic acid ↔mono - acetin + water

Monoacetin + acetic acid↔ diacetin + water

Diacetin + acetic acid ↔ triacetin + water

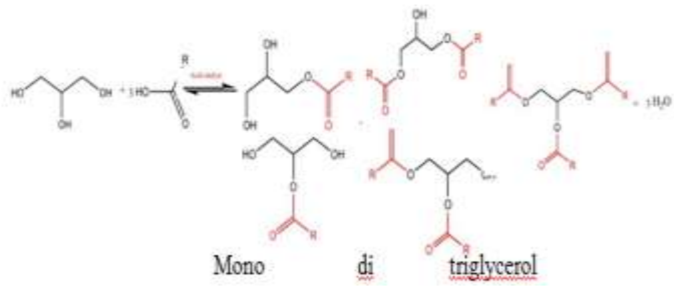


Fig 2: Conversion of glycerol to glycerol esters

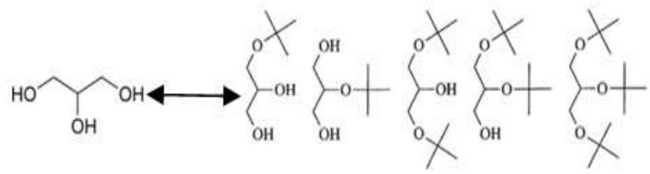
Similarly glycerol esterification with oleic acid can produce mono, di and tri- oleate. Glycerol esterification processes are carried out using mineral acids, acidic heterogenic catalysts (immobilized sulfonic acid groups, zeolites, niobic acid, polyvinyl sulfonic resins, sol gel based sulfated zircona, fluro-sulfonic acid functionalized mono-structured silica (SBA), solfonated carbon based materials etc, have all demonstrated excellent catalytic behavior (Lopes et al. 2015, Sepulveda et al, 2015). Acetylation of glycerol with bimetallic silver and copper deposited rice husk silica-alumina was experimented by Ramalingam et al, 2016, and reported conversion rate of 98% with 51% selectivity towards diacetin and tri-acetins.

Triacetin also known glycerol triacetate(TAG) an excellent solvent finds application as a plasticizer for cellulosic acetate, vinylidene, ethyl cellulose, nitrocellulose and copolymers. Glycerol diacetate(DAG) and TAG have are promising components as bio-additives for liquid fuels.TAG is known to increase octane number, viscosity properties, reduce cloud point, cold flow properties and can be an alternative to controversial tertiary alkyl ether as fuel-additive. Zirconia supported heteropoly acids, sulphonated zirconia catalysthave been extensively used for TAG production with high yield.

4. ALKYLATION OF BIO-GLYCEROL/ ETHERIFICATION OF GLYCEROL

Oxygenated gasoline such as methyl tertiary butyl ethers

(MTBEs) have been in demand. They are highly toxic and are not easily biodegradable. Glycerol tertiary butyl ether (GTBE) is an oxygenated fuel that can potentially replace MTBEs and have been explored for improved emissions. (Noureddini et al. 1998).Alkylation of glycerol can be performed with etherifying agents such as isobutylene, C4 olefinic petrochemicals and butyl alcohol. Tert-butyl ethers of glycerol when blended with diesel fuels, emissions of particulate matter, carbon monoxide, hydrocarbons and unregulated aldehydes decrease significantly.Eterification with isobutylene, mixtures of mono, di and tri GTBE are obtained and only di and tri GTBEs qualify as lubricants. Reaction is as shown in Figure: 2. Heterogeneous catalysts such as acidic ion-exchange resins, Amberlyst 15 and 35, pore zeolites such as H-Y, H-Beta, pillared clays, solfonated niobia, Pt-SBA-15, sulfonic meso structured silicas etc (Kong et al, 2016). Poly glycerols are also oxygenated compounds obtained by etherification process with lineal, branched and cyclic chains such as GTBE, methyl tertiary butyl ether, 1,3 di- tert butyl glycerol, 1, 2 –di-tertbutyl glycerol 1,2,3-tri –tert butyl glycerol(Bagheri et al, 2015, Mukhopadhyay et al, 2015). They are non –ionic surfactants and can stabilize emulsions and suspensions. They are widely applied as cosmetic ingredients, lubricants, polymer additives, nutritional additives



etc. Mixed oxides (MgFeO, MgAlO), LiOH modified monomorillonite K-10 (Li/MK-10), microwave radiation have all accelerated glycerol conversion to polyglycerols. Microwave radiation treatment in a catalyst free environment showed 100% conversion with 50% selectivity towards diglycerols. The conversion was attributed to presence of soap in crude glycerol and a patent application was filed by Malaysian Palm Oil Board (Hoong et al, 2014)

5. OUTLOOK AND CONCLUSIONS

Biodiesel production is projected to grow worldwide and researchers are focusing on new alternatives in using crude glycerol produced. The glycerol glut presents challenges to the existing producing plants with reduced economy and also offers excellent opportunities to produce avariety of platform chemicals that are highly valued such as DHA, 1,3-PD, acrolein, hydrogen, ethanol, etc. In this review paper, we have presented different catalysts employed and processes that have resulted in production of various bio-additives in the form of glycerol ethers and esters and have aimed to provide an insight to various terminologies used for the same compound. Fuel additives obtained by these processes, thus when blended should be able to address diesel fuel properties - Cetane numbers (low cetane numbers exhibit long ignition delay, abnormal combustion) Cold flow improver, improved lubricity, reduced smoke emission, mitigate NOx emission with reduced CO and HC emission and cold flow properties.

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