RESEARCH REVIEW ON SOLID ACID CATALYSED FOR GLYCEROL ETHERIFICATIONS

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ABSTRACT

The improvement of elective impetuses for etherification, which have high movement, high profitability, and simple recuperation without extreme natural contamination, is the developing themes concerning the part of the green-concoction forms. Glycerol etherification with tert-butanol produces water as result while isobutene is not. The high extremity of the reactants, and by water delivered into response, incites draining of the impetus, trading off the means of recuperation and reuse, and bringing about defilement of the items. For hetero poly corrosive impetus, for example, phosphotungstic or silicostungstic corrosive, the movement and strength of the impetuses rely upon the structure and the kind of the focal iota alongside the metal. The silicotungstic corrosive mass (STAB) impregnated onto diverse backings, for example, polymers and silica to accomplish high surface region and soundness in polar solvents. Ionic fluids (IL) are salts that are fluid at low temperature and when in the liquid shape made completely out of particles. Their flexible properties make ILs great solvents and impetuses in concoction responses. This investigation inspects the latest advancements in particular synergist transformation of glycerol to promising product synthetic substances and powers. This investigation concentrated on the etherification of glycerol with tert-butyl liquor over various strong corrosive frameworks. Consideration offered principally to examine the primary constraining variables for expansive scale process improvement.

Keywords: *Green chemical process, Leaching, Polar solvents, Catalytic Conversion.*

1. INTRODUCTION

These vitality emergencies, ecological issues and exhaustion of the world's oil saves help the creation and utilization of sustainable powers. Biodiesel is getting expanded consideration as an option, non-harmful and biodegradable sustainable fuel[1]. At present sustainable power source commitment is just 13.3% while non-renewable energy sources are contributing 86% (36% oil, 27% coal and 23% gaseous petrol) of the worldwide vitality request. The biodiesel generation in 2010 was 20 million tons and it is required to achieve 150 million tons by 2020[2], [3]. As indicated by the new vitality enactment (Directive 2009/28/EC) which has proclaimed in Europe transportation powers ought to contain 10% from inexhaustible sources by end of 2020[4]. Biodiesel contributes less to a dangerous atmospheric deviation than non-renewable energy sources because of the decrease of CO2, CO and hydrocarbon discharges from the motor [5]. Glycerol is the fundamental result in the trans-esterification response that can be acquired 10 m3 for every 90 m3 of biodiesel created. One mole of glycerol conveyed as a co-thing for every three moles of methyl ester (biodiesel) which is proportionate to around 10 wt. level of the total thing. The overall biodiesel exhibit assessed to reach 37 billion gallons up to 2016. About, four billion gallons of foul glycerol is conveyed[6]. Mean money related of biodiesel age vehemently depend on fruitful utilization of the outcome glycerol. The availability of the alkyl ethers of glycerol by etherification (0-alkylation) by alkenes, and particularly by isobutylene, or C4-division from pyrolysis and FCC at the proximity of the destructive stimulus is one of the possible results of the glycerol use.

The mix of mono-, di-and tri-alkyl glycerol ethers made. These ethers and generally di-and tri-alkyl glycerol's are the most sensible as oxygenates to diesel fills. The development of these ethers has valuable result on the idea of definitive diesel fuel (high CN) and uncommonly ethers are dynamic by decline of vapor and particulate issues, carbon oxides and carbonyl blends in cripples[7]. Generally speaking, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME) are used as included substances for diesel, these can be incorporated biodiesel also. These additional substances conveyed from non-unlimited non-sustainable power source resources like oil. The oil derived fuel included substances are over the top and cause common defilement, so there is wide research in headway to convey fuel included substances from elective imperativeness sources, for instance, glycerol. Usage of lead was confined in 1995 (United States), and after that methyl tert-butyl ether (MTBE) was used as an additional substance rather than TEL. MTBE reduces the carbon monoxide surge from fuel anyway it is exceedingly dissolvable in water and can pollute drinking water. MTBE is causing disease-causing ramifications for animals. Finally it was in like manner limited in 2001 by Environmental Protection Agency (EPA) at United States, by and by ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME) are used as included substances for diesel, anyway these are subordinates of oil [6]. Better execution of diesel motor is the diesel having cetane number among 40 to 51. Biodiesel from vegetable sources have recorded as having a cetane number range 48 to 61. Powers with higher cetane number, which have shorter start delays, give more opportunity to the fuel procedure ignition is to be finished[8]. Glycerol can changed over into advantage synthetic concoctions by various reactant forms including improving, oxidation, hydrogen lysis, etherification, acetylating or etherification and so on.[3], [9], [10].

Another probability to valorize glycerol is its change into oxygenated added substances for fluid fuel applications. Distinctive glycerol based mixes, for example, glycerol ethers, acetyls glycerol and glycerol acetyl have recognized as important substitution of ordinary fuel added substances, which rely upon exhausting oil sources, their value vulnerability, and developing ecological worry of oil feed stock[9]. Etherification of glycerol is one of a promising procedure for oxygenate fuel generation. The items from etherification of glycerol with tert-butyl liquor comprises of mono-, di-and tri-tert-ethers of glycerol. Mono-tert-butyl ether of glycerol has a low solvency in diesel fuel and in this manner the etherification of glycerol must coordinated to the extreme arrangement of di-and tri-ethers. Since the blend of ethers is a common case of balance constrained response that produces result H2O. The nearness of H2O has a solid hindrance impact on the reactant action and change is commonly low because of points of confinement forced by thermodynamic balance[8]. As the rate of response, utilizing essential impetus is a lot quicker than that catalyzed by the corrosive impetus; fundamental impetuses utilized frequently economically. To acquire esteem included items from glycerol numerous ventures are utilizing customary mineral corrosive impetuses, which have low selectivity. Accordingly, reason for the investigation is to utilize strong corrosive impetuses, which results in high selectivity and transformation to valorize glycerol into esteem added synthetic concoctions and to expand most extreme utilization of sustainable assets.

The consolidation of oregano sulfonic bunches over meso-organized silica's has produced compelling strong corrosive impetuses with upgraded synergist properties as contrasted and ordinary homogeneous and heterogeneous corrosive impetuses. Specifically, tert-butyl ethers of glycerol with a high substance of di-ethers considered promising as oxygenated added substances for diesel powers (diesel, biodiesel and their blends). Be that as it may, mono-tert-butyl ethers of glycerol (MBGEs) have a low solvency in diesel fuel; in this way, so as to maintain a strategic distance from an extra division step, the etherification of glycerol 1 should address the arrangement of di-and tri-ethers[11]. Glycerol etherification responses can performed with various olefins and alcohols, principally Isobutylene and tert-butyl liquor. Etherification responses of glycerol by tert-butyl liquor can completed in the fluid stage without a dissolvable, and tert-butyl ethers of glycerol can be broken up in the response blend[12].

1.1 Importance of additive presence in fuel:

The main role of fuel added substance is to upgrade octane/cetane number by enhancing the counter thumping property of fuel. In mid-1920's tetra ethyl lead (TEL) was utilized as an added substance yet it frees lead into air which drives natural and medical issues by influencing the neural conduct and furthermore causing hypertension in grown-ups[13]. [7].

The use of biodiesel has certain difficulties. Biodiesel has polyunsaturated segment, has propensity towards polymerization, and structures a long chain particle. It is hard to pass the long chain atom through fuel channel, so it amasses and frames a gum like materials.

Cloud purposes of diesel and biodiesel were - 16°C and 0°C. Lower cloud point was favored for better execution of the fuel [7]. To decrease the cloud point and limit the polymerization included substances required. As a rule, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME) are used as included substances for diesel, these can be incorporated biodiesel also.

These additional substances made from non-reasonable non-sustainable power source resources like oil. The oil decided fuel included substances are excessive and cause characteristic tainting, so there is wide research in progression to convey fuel included substances from elective essentialness sources, for instance, glycerol. Glycerol ethers conveyed from etherification of glycerol with an alcohol. Extension of glycerol ether can decrease particulate issue and risky gas releases from biodiesel oil [7], so it helps to prevent the environmental pollution.

1.2 Influence of acidity and pore volume on glycerol etherification reaction:

According researcher acridity assumes a critical job in etherification. Distinctive kinds of Amberlyst impetuses (Amberlyst-15, Amberlyst-35 and Amberlyst-36 with acridity scopes of 4.2-5.6 mmol/g demonstrated great execution than different impetuses because of their higher acidic nature. The Bronzed acidic locales can discharge proton (H+) into the response blend, which is profoundly receptive and it responds with OH gathering of liquor and structures water. The protonated liquor responds with glycerol and structures mono glycerol ether. Along these lines, the degree of mono ether development relies upon the causticity of the impetus, and after that the arrangement of etherification responses. [14], [15]

Depend on the available active sites of the catalyst[16]. The usage of commercial catalysts was limited due to its surface area (53 m^2/g) and lack of thermal stability. Hetero poly acids are highly acidic in nature and thermally stable[17], so the fuse of these can build up the acidic locales on the help. So higher pore volume wanted to suit more measure of Hetero polynacids. Glycerol change straightly expanded with increment in temperature and impetus/glycerol weight proportion. There was no item seen with no impetus and a huge glycerol ether development could saw as the measure of impetus expanded.

2. Methodology adopted by researchers

2.1 Mechanism of Glycerol Etherification:

At the point when Glycerol responds with tert-butanol (TBA), it produces Ether and water. Within the sight of Acidic and permeable impetus, the adsorbed TBA on the impetuses surface can discharge the proton (H+) into the response blend. These protonated atoms are exceedingly receptive and they respond with glycerol to shape mono-tert-butyl glycerol ether and water.

Mono-tert-butyl glycerol adsorbed on impetuses surface and experiences further etherification to deliver di-and tri-tert butyl glycerol.

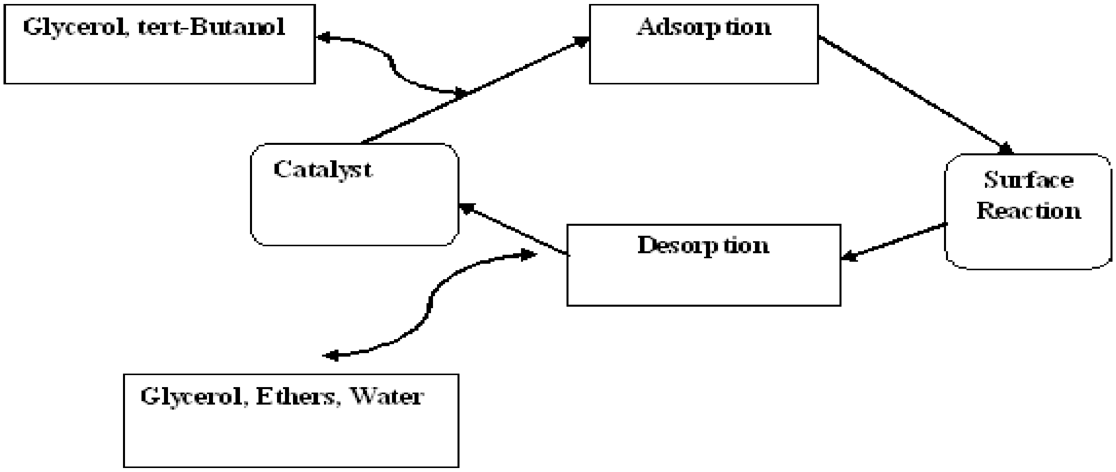
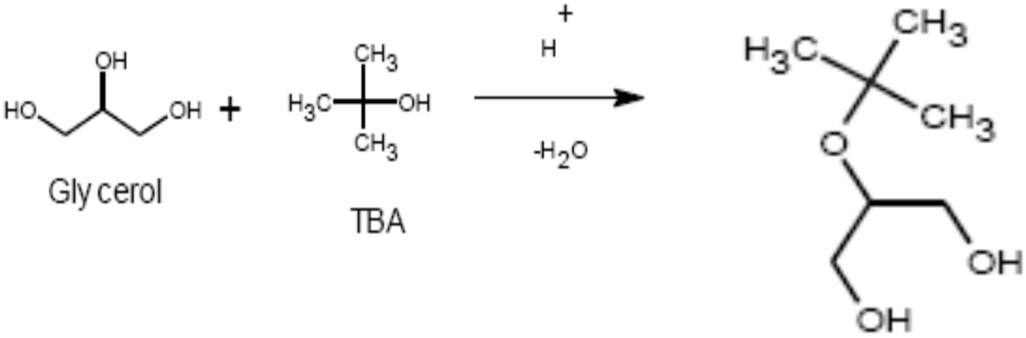
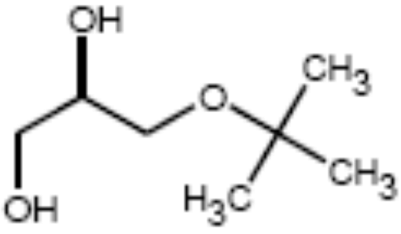


Fig. 2.1: Mechanism of glycerol Etherification

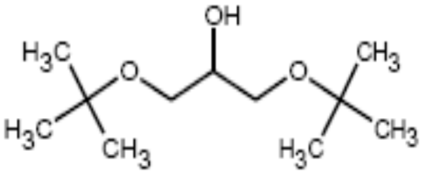
2.1.1 Reaction Scheme:



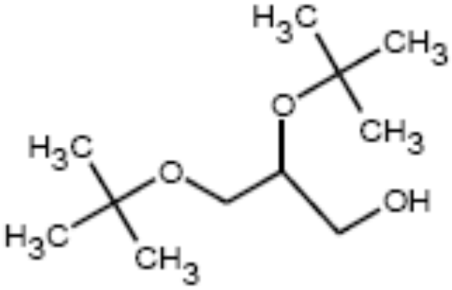
MTBG-1 (3-tert-butoxy-1, 2 propanodial) :



MTBG-2 (2-tert-butoxy-1, 3 propanodial) :



DTBG-1 (2, 3 di-tert-butoxy-1propanodial) :



DTBG-2 1, (3 di-tert-butoxy-2 propanodial) :

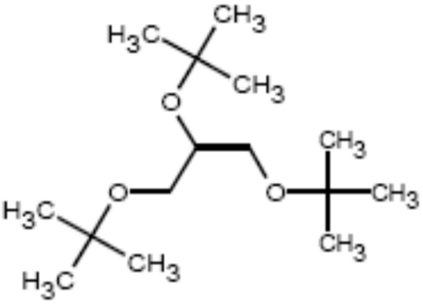


Fig. 2.2: Reaction Scheme [6]

2.2 Kinetics of Etherification:

Langmuir- Hinshelwood Kinetics:

Glycerol Etherification with TBA controlled by

1) Adsorption
2) Surface reaction
3) Desorption

Glycerol: G, TBA: T, Catalyst: X, MTBG: C, Water: D

Step 1: Adsorption of glycerol on catalyst surface

Catalysts require higher surface area for adsorption because of Glycerol is highly viscous. Glycerol (A) and tert-butyl alcohol (B) gets, adsorbed on active sites of catalyst surface as shown in equation 1 and equation 2 respectively.

A + X = A.X ---------------------- (1)

B + X = B.X ---------------------- (2)

Step 2: Surface Reaction of adsorbed Glycerol and TBA

Adsorbed Glycerol (A.X) and TBA (B.X) undergo surface reaction and form mono glycerol ether (C.X), water (D.X) as product and co-product as per the equation 3. To induce surface reaction between two adsorbed molecules requires Bronsted acidity. Therefore, acidity of the catalysts is responsible for the surface reaction. Higher pore volume of the catalysts is required to avoid diffusional resistance.

A.X + B.X = C.X + D.X ------------- (3)

Step 3: Desorption of MTBG and water

MTBG and water produced by surface reaction held on the catalyst surface. These products desorb and detach from the catalysts surface. The active sites (X) of the catalyst are available for further etherification as in equation 4 and 5. The active sites adsorb fresh Glycerol and product mono ether undergoes further etherification and produces di and tri Glycerol ethers. So the extent of bulk ethers adsorption depends upon the porosity of the catalyst. Highly porous catalysts can absorb mono ethers and which undergoes further etherification. The catalysts play an important role in extent of etherification. For more conversion of glycerol, catalyst is required with acidity and higher pore volume.

C.X = C + X ------------------------ (4)

D.X = D + X ------------------------- (5)

$$\text{Glycerol Conversion} = \frac{\text{Moles of Glycerol reacted}}{\text{Moles of glycerol taken}} \text{X100}$$

$$\text{DTBG Selectivity} = \frac{\text{Moles of DTBG Produced}}{\text{Total Moles of Product}} \text{ x } 100$$

$$\text{DTBG Yield} = \frac{\text{Moles of DTBG Produced}}{\text{Moles of glycerol taken}} \text{ x } 100$$

2.3. Types of Catalysis:

On the off chance that the impetus and reactants or their answer frames a typical physical stage, at that point the response called homogeneously catalyzed. Metal salts of natural acids, organometallic buildings, and carbonyls of Co, Fe, and Rh are commonplace homogeneous impetuses. Instances of homogeneously catalyzed responses are oxidation of toluene to benzoic corrosive within the sight of Co and Mn benzoates and hydro-formylation of olefins to give the relating aldehydes. This response catalyzed via carbonyls of Co or Rh. Heterogeneous catalysis includes frameworks in which impetus and reactants shape separate physical stages. Average heterogeneous impetuses are inorganic solids, for example, metals, oxides, sulfides, and metal salts, however they might be natural materials, for example, natural hydro peroxides, particle exchangers, and proteins.

Instances of heterogeneously catalyzed responses are alkali combination from the components over advanced iron impetuses in the gas stage and hydrogenation of palatable oils on Ni – kieselguhr impetuses in the fluid stage, which are instances of inorganic and natural catalysis, individually.

Electro catalysis is an uncommon instance of heterogeneous catalysis including oxidation or decrease by exchange of electrons. Models are the utilization of chemically dynamic anodes in electrolysis procedures, for example, chloro salt electrolysis and in power devices. In photographs, the impetus or a reactant ingests catalysis light amid the response. This can occur in a homogeneous or heterogeneous framework. One precedent is the usage of semiconductor impetuses (titanium, zinc, and iron oxides) for photochemical corruption of natural substances, e.g., on self-cleaning surfaces.

In biocatalysts, chemicals or microorganisms catalyze different biochemical responses. The impetuses can immobilized on different bearers, for example, permeable glass, SiO2, and natural polymers. Noticeable instances of biochemical responses are isomerization of glucose to fructose, critical in the generation of sodas, by utilizing compounds, for example, gluco-amylase immobilized on SiO2, and the transformation of acrylonitrile to acrylamide by cells of coryne-microbes ensnared in a polyacrylamide gel. The primary point of ecological catalysis is natural security. Precedents are the decrease of NOx in stack gases with NH3 on V2O5 – TiO2 impetuses and the expulsion of NOx, CO, and hydrocarbons from car fumes gases by utilizing the supposed three-way impetus comprising of Rh – Pt – CeO2 – Al2O2 saved on fired honeycombs.

The term green synergist forms has been utilized as often as possible as of late, inferring that substance procedures might be made naturally kindhearted by exploiting the conceivable exceptional returns and selectivity's for the objective items, with next to zero undesirable side items and furthermore frequently high vitality effectiveness. The essential concoction standards of catalysis comprise in the coordination of reactant particles to focal iotas, the ligands of which might be sub-atomic species (homogeneous and bio catalysis) or neighboring molecules at the surface of the strong grid (heterogeneous catalysis). In spite of the fact that there are contrasts in the subtleties of different kinds of catalysis (e.g., solvation impacts in the fluid stage, which don't happen in strong – gas responses), a closer and without a doubt productive joint effort between the different networks speaking to homogeneous, heterogeneous, and bio catalysis ought to be unequivocally bolstered. Articulation by David Parker (ICI) amid the 21st Irvine Lectures on 24 April 1998 at the University of St. Andrews ought to be referenced in this association, in particular, that,"At the sub-atomic dimension, there is little to recognize homogeneous and heterogeneous catalysis, however there are clear qualifications at the mechanical dimension"[1]

Summary of Literature review on etherification of glycerol using different catalyst

Catalyst	Reactant	Acidity (mmol H^+/g)	SBET m2/g	Reaction temp	Catalyst wt%	Reaction time (hr)	Glycerol conversion	Ethers selectivity		Ref.
								Mono	h-GTBE Di+ Tri	
Amberlyst-15	Glycerol, tert-Butanol	4.7	53	60	7.5	8	79	81.3	18.7	[12]
Amberlyst-15	Glycerol, tert-Butanol	4.7	53	75	5	24	81	64	36	[12]
Amberlyst-15	Glycerol, iso-Butylene	4.7	53	90	7.5	8	50.2	71.5	28.5	[12]
Amberlyst-35	Glycerol, iso-Butylene	5.2	50	60	7.5	8	86	84.4	15.6	[12]
Amberlyst-35	Glycerol, tert-Butanol	5.2	53	90	7.5	8	68.6	75.8	24.2	[12]
Amberlyst-36	Glycerol, iso-Butylene	>5.40	33	150	5	4	-	-	-	[18]
H-Mordenite zeolite (Si/Al=6.9)	Glycerol, tert-Butanol	0.18	-	75	5	24	29	78	22	[16]
H-Beta zeolite (Si/Al=11)	Glycerol, iso-Butylene	0.60	681	75	5	6	55	70	30	[16]

H-Beta zeolite (Si/Al=11)	Glycerol, tert-Butanol	0.60	633	75	5	24	66	66	34	[16]
H-ZSM-5 zeolite (Si/Al=20.2)	Glycerol, tert-Butanol	0.37	-	75	5	24	58	96	4	[16]
Cs-HPW	Glycerol, tert-Butanol	0.81	81	70	7.5	6	50	-	-	[17]
H-Y (CBV-720)	Glycerol, tert-Butanol	0.56	697	90	7.5	8	88.7	-	-	[14]
HPW-17	Glycerol, tert-Butanol	0.74	200	90	15	6	85	-	-	[11]
Cs-HPW	Glycerol, tert-Butanol	0.81	207	90	0.5	6	85	-	-	[11]
SAC-13	Glycerol, tert-Butanol	0.15	189	90	13	6	84	-	-	[11]
Mont-KSF/O	Glycerol, tert-butyl alcohol	0.015	128	110	27.17	6	70	87	12	[19]

Table2.3 Reported results of etherification of glycerol by several researchers

2.4 Physical Properties of reactants and products:

Component	Mol. Formula	Mol. Weight g/mol	Boiling point 0c	Density g/cm^3
Glycerol	$C_3H_8O_3$	92.09	290	1.26
TBA	$C_4H_{10}O$	74.12	82.2	780.90
MTBG	$C_7H_{18}O_4$	166		
DTBG	$C_{11}H_{26}O_4$	222	100-102 ^{0}C	
TTBG	$C_{15}H_{34}O_4$	278		

Table 2.4 Physical Properties of reactants and products

2.5 Applications of Glycerol Based Products:

Glycerol Based products	Applications
Monoacetin	Used in cryogenics
Diacetin	Used as raw materials of biodegradable polyester.
Triacetin	Used in cosmetics and fuel additive
Glycerol mono- acetate	Cryogenics and polymers.
Glycerol tri- acetate.	Cold flow improver, viscosity reducer, for biodiesel octane booster, for gasoline as an alternative for commercial alkyl ethers.

1,2- Propanediol	Formulated into composites, adhesives, laminates, powder and by curd coating, co-polyester, anti-freeze, solvent, corterra polymers
Acrolein	Used as micro biocide in oil wells liquid hydrocarbon fuels water treatment ponds, slimicide in manufacture of paper
Mono-acetyl ester	Cryogenics
Di-acetyl ester	Production of biodegradable. Polyesters
Tri-acetyl ester	Fuel additive
Olefins	Polymer precursors
Gasoline Precursors	Alkylation reaction

Table 2.5 Application of Glycerol Based Products

CONCLUSIONS

The invention modification of glycerol with a liquor can deliver glycerol ether. These are the swaps for oil determined fuel added substances. Along these lines, this procedure can build the glycerol advertise, which is practical to the diesel and biodiesel enterprises. The target of this work was to build up an impetus for the successful use of glycerol by changing over to glycerol ethers. Etherification of glycerol with tert-butanol can viably occur within the sight of strong corrosive impetus. The required impetus was set up with the impregnation of Hetero poly acids on permeable help, on the grounds that Hetero poly acids were profoundly acidic in nature, its quality can upgraded the number and acidic quality of the acidic locales on help. Glycerol etherification with iso-butylene adequately accomplished within the sight of different impetuses. Among all impetuses Amberlyst-15 catalyzed the etherification response all the more successfully at the temperature of 90oC having less response time of 8 hr and transformation of glycerol was observed to be 50.2% with greatest selectivity of ~29% to DTBGE.

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