

Preface

Starting from powering engines to lighting the lamps, fossil fuels have become indispensable part of human life. The use of biofuels like ethanol, butanol and biodiesel as an energy alternative has become a hot topic within the scientific community as it augments in cutting down the greenhouse gas exhausts concurrently providing energy security for the future generations. According to World Bioenergy Association, Europe, United States and Asia are principal producers of liquid biodiesel. Biodiesel is fatty acid methyl esters (FAME) produced from transesterification reaction of oil, algae or animal derived triglycerides and a monohydric alcohol. However, the production cost of biodiesel is relatively high and leads to co-generation of a major co-product 'glycerol' (10 wt.% of total produce). Glycerol is cheap and highly reactive triol which makes it a potential green platform chemical for the synthesis of broad spectrum value added products. Proper utilization of surplus glycerol is a promising transformation as a small portion of it has direct commercial applications, hence exploration of a smart, sustainable, and profitable way of glycerol conversion to value added downstream products like 1,2 or 1,3 diols, dihydroxy acetone, ethylene glycol, mono/di/tri glycerol ethers, hydrogen, glycerol carbonate etc. is vital. Over the recent years, catalytic conversion of glycerol into cyclic carbonate of glycerol i.e., glycerol carbonate (GlyC) has increased tremendously due to its unique properties like biodegradability, water solubility, low toxicity, and low volatility. These properties of glycerol carbonate are used in beauty and personal care industries, as carrier solvents in pharmaceutical industries, surfactants, carrier in lithium-ion batteries, component in membranes for gas separation equipment. Most importantly, the presence of both carbonyl and hydroxyl functionalities makes GlyC a precursor for synthesis of a variety of polymers including polyesters, polyurethanes, and polycarbonates. The conventional synthesis of glycerol carbonate can be carried out through different pathways depending on the carbonyl source in feed which may include phosgene, urea, carbon monoxide

(CO) and carbon dioxide (CO₂). But these routes have certain drawbacks like in glycerolysis using urea feed requires continuous removal of ammonia from the reaction system and the formation of isocyanic acid, biuret decreases the rate of GlyC formation and makes the process less desirable. In glycerol carboxylation using CO₂ requires high pressure and temperature conditions but provides very low glycerol carbonate yield which greatly increases the production costs. Direct synthesis of glycerol carbonate through transesterification of glycerol and dimethyl carbonate is considered to be the best green pathway as it involves no side reactions, no by-products and the reaction proceeds in equimolar ratios, easy separation of catalyst, etc. The transesterification reaction is catalysed by catalyst having appreciable number of active basic sites for the activation of a glycerol molecule. The activated glycerol undergoes nucleophilic addition reaction with activated dimethyl carbonate to give a molecule of glycerol carbonate. Using a suitable catalyst under optimal conditions, for the transesterification process boosts up the yield of desired GlyC by chemically activating the reactant species and increasing the reaction rates. Homogeneous bases like potassium (K), sodium (Na) or calcium-based carbonates, alkoxides, hydroxides, and organic ionic liquids (ILs) have already been used for the transesterification process. The major drawbacks of using such homogenous catalysts are the difficult separation procedure after the reaction and leaching of the catalyst contents during the reaction process. Hence, the use of such catalysts is discouraged. Lately, the use of solid base heterogeneous catalyst has gained much prevalence. Literature showed successful application of mixed metal oxides as effective heterogeneous catalysts for transesterification. Mainly, both alkali and alkaline earth metal oxides are highly basic in nature and influence the transesterification reaction of glycerol. As a results investigations were carried out on influence of alkaline earth metal oxides on transesterification reaction of glycerol on the basis of catalyst concentration, reaction temperature, reaction time, glycerol to DMC molar ratios.

This thesis includes study on synthesis of Transition metal based heterogeneous catalysts and their application in synthesis of glycerol carbonate, physicochemical properties study of designed catalyst, optimization study of entire reaction process, both qualitative and quantitative study of glycerol carbonate and reusability study of catalyst.