CHAPTER 7

Catalytic Glycerol Transformation to Value-added Chemicals

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7.1 INTRODUCTION

The idea of catalytic glycerol transformation to value-added chemicals has been discussed ever since the rapid production of biodiesel (Luo et al., 2016; Bagheri et al., 2015; Veluturla et al., 2018). Catalytic conversion of glycerol to value-added chemicals has emerged as another essential and potential process to be profitable (Muraza, 2019). This occurred in view of the abundance of availability and rock bottom price of glycerol in the market (Paillet et al., 2019). Several reactions involving the catalytic transformation of glycerol to precious chemicals such as hydrogen (Ghani et al., 2018), acrolein (Possato et al., 2017), propylene glycol (Freitas et al., 2018), dihydroxyacetone (Ning et al., 2016), glycerol carbonate (Marimuthu et al., 2018), epichlorohydrin (Kong et al., 2016), glycerol ether (Nandiwale et al., 2014), olefins (Zakaria et al., 2014a) and others were widely reported. Nonetheless, the ultimate issue is the feasibility of the overall process to be commercially viable. Many of the processes are not in optimum state to be invested with. Aspects such as the fundamental chemistry, catalyst design and stability, process, reactor development, modelling, and simulation works are still lacking. More investigations need to be performed to seek and establish a profitable pathway for catalytic conversion of glycerol to its derivatives. The objective of this mini-review is to examine the available processes for catalytic conversion of glycerol to important chemicals with consideration of utilizing refined and crude glycerol. Associated features within the processes such as catalyst selection, process parameters, reactor selection, feasibility of study and economic potential are detailed out. Finally, discussion on the challenges, opportunities and direction follow suits.

7.2 GLYCEROL

Glycerol, a trihydric containing three hydroxyl groups (Figure 7.1), is a very important chemical compound for various industrial applications. It is a kind of monomer of the majority natural polyols, together with starch, cellulose, hemicelluloses, and other carbohydrate polymers (Quispe et al., 2013). Glycerol, non-toxic, biodegradable, and recyclable liquid manufactured from renewable sources, has high potential to be an alternative green solvent for organic reactions (Pagliaro & Rossi, 2008).

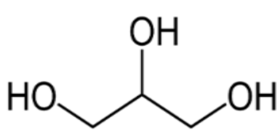

Figure 7.1 Glycerol chemical structure

Glycerol is a valuable by-product of biodiesel production with a refined value close to USD 1.0 kg^{-1} (Monteiro et al., 2018). Biodiesel is currently produced by transesterification of vegetable oils (triglycerides) and methanol, with 1 mol of glycerol produced per mol of triglyceride feed. As biodiesel production increases, the price of glycerol is expected to drop significantly from the actual cost which has already decreased by half in the last few years. It has been observed that the cost of crude glycerol since 2001 has decreased 25-40% to between USD 0.35kg-1 and USD 0.45kg-1 in 2010 (Zakaria et al., 2013). Although this contributed to a drastically low price of glycerol, the cost of producing biodiesel is still high. The higher cost of biodiesel is primarily due to the raw material cost (Zahan & Kano, 2018). Despite credit received from the reselling of crude glycerol, based on 2010 National Renewable Energy Laboratory (NREL) report, the economics of biodiesel production may be improved if value-added chemicals can be produced from glycerol (Rodrigues et al., 2017). Such an inexpensive feed makes the process development for the conversion of glycerol into other chemicals desirable.

Glycerol is mainly produced from high-pressure splitting in the oil and fats industry (Yeong et al., 2012), soap production via the saponification process (Tan et al., 2013) and biodiesel production (Ganigué et al., 2019). Among all the processes, the manufacturing of biodiesel appeared to be the dominating contributing source for the production of glycerol as shown in Figure 7.2. This occurred due to the rapid increasing demand of worldwide biodiesel production as illustrated in Figure 7.3. With increasing biodiesel production, the accompanying by-product, which is glycerol, also increases. Consequently, the cost of crude glycerol dropped and became economically attractive. This offers glycerol as a popular feedstock for its upgrading to precious chemicals.

Purification of crude glycerol will yield a more expensive refined glycerol. Earlier, extensive studies were made on the catalytic conversion of refined glycerol to value-added chemicals (Wang et al., 2019b; Ye & Ren, 2014; Bagheri et al., 2015; Kong