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Review

A perspective on catalytic conversion of glycerol to olefins



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ABSTRACT

Glycerol, an alcohol and oxygenated chemical from biodiesel production, has enormous potential to be converted into higher value-added fuels and chemicals. Conversion of glycerol to olefins, although relatively new, has been proven viable by the limited number of literatures available. However, the studies on alcohol-to-hydrocarbons involving methanol and ethanol conversions to hydrocarbons (MTHC and ETHC) have extensively been conducted. Due to the increasing amount of glycerol produced worldwide and the importance of olefins in the industry, it is therefore essential to have broadened knowledge on the technology of glycerol conversion to olefin (GTO). This review focuses on GTO with reference to the more established MTHC and ETHC studies. The chemistry and reaction schemes for methanol and ethanol reactions to produce hydrocarbons are also reviewed to provide some basics study for GTO. Catalytic conversion processes with different raw materials for obtaining olefins are then compared with GTO. GTO offers viable, sustainable and environmental friendly technology for green olefins production from renewable resources, and concerted efforts should be geared to explore its potential.

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1. Introduction

The notion of catalytic glycerol conversion to important chemicals and fuel is not new [1]. Recently, catalytic conversion of glycerol to olefins has emerged as another essential and potential process to be profitable [2,3]. Unfortunately, very limited studies regarding it have been reported. Several reaction schemes have been proposed [2,4,5] but the optimum process is yet to be discovered. Other aspects such as catalyst selection and chemistry, process, reactor development, modeling and simulation works are also still lacking. More

investigations need to be performed to seek and establish the best reaction pathway for catalytic conversion of glycerol to olefins. The objective of this review is to carefully examine the processes available for catalytic conversion of glycerol to olefins published recently. Associated features within the processes such as catalyst selection, reaction mechanism, process parameters, reactor selection, feasibility of study and economic potential are detailed out. Being relatively a new process, glycerol to olefins is compared with the established methanol/ethanol to olefins/paraffins in order to comprehend the basic sciences and engineering involve.

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2. Glycerol

Glycerol, a trihydric containing three hydroxyl groups, 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 [3]. Glycerol, non-toxic, biodegradable and recyclable liquid manufactured from renewable sources, has high potential to be an alternative green solvent for organic reactions [6–8]. Table 1 lists the basic physical and chemical properties of glycerol.

Glycerol is a valuable byproduct of biodiesel production with a refined value close to 1.0 \$ kg⁻¹ [9]. Biodiesel is currently produced by transesterification [10] (Fig. 1) of vegetable oils (triglycerides) and methanol, with 1 mol of glycerol produced per mol of triglyceride feed [11,12]. 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 [9,13,14]. Thus, it has been estimated [15] and proven [16] that the cost of unrefined glycerol since 2001 has decreased 25–40% to between 0.35 \$ kg⁻¹ and 0.45 \$ kg⁻¹ in 2010. 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 [17]. Despite credit received from the reselling of crude glycerol, based on 2010 National Renewable Energy Laboratory (NREL) report [18], the economics of biodiesel production may be improved if value-added products such as hydrogen, synthesis gas, liquid chemicals or olefins can be produced from byproduct glycerol. Such an inexpensive feed makes the process development for the conversion of glycerol into other fuels and chemicals desirable.

3. Glycerol transformation into valuable products

As glycerol is already a highly functionalized molecule compared to hydrocarbons, it has the advantage to be used as feedstock for the production of valuable products. Glycerol can be converted to other valuable products biologically [19,20] and chemically [21]. The use of bacteriologic transformation of glycerol also has been proven for the production of fuels and chemicals [21], cosmetic applications [22], succinic acid [23] and citric acid [24] for food and pharmaceutical industries, polyhydroxyacanoate for medical and agricultural

field [25] as well as other products for basic chemical applications.

The unique structure of glycerol makes it possible to conduct heterogeneous catalytic oxidation reaction using cheaper oxidizing agent such as air, oxygen and hydrogen peroxide [21]. Some of the processes include selective oxidation [26,27], hydrogenolysis [28,29], dehydration [30,31], acetylation [32], carboxylation [33,34], pyrolysis [35], gasification [36], dehydroxylation [37], steam reforming [38], esterification [39,40] and etherification [41–44]. Among the chemical reactions that draw the interests of many researchers are the transformation of glycerol into fuel oxygenates by etherification and esterification since these reactions are economically beneficial to the production of glycerol byproducts and biodiesel process. In addition, the catalytic conversion of glycerol to olefins is drawing great interest due to the feasibility of the process and the possibility of obtaining olefins from a renewable source.

4. Olefins

Olefin is a family of unsaturated aliphatic hydrocarbons having the general formula C_nH_{2n} [45,46]. It is an unsaturated chemical compound [47] containing at least one carbon-to-carbon double bond hence, are chemically reactive [46,47]. Having such properties, olefin is a very important component to manufacture endless end use products.

Light olefins consisting of ethylene, propylene and butylenes together with benzene, toluene and xylenes (BTX) are the most important petrochemical building blocks for making petrochemicals and polymers such as polyethylene, polypropylene, polyvinyl chloride (PVC), ethylene glycol and rubber [48,49]. Light olefins are mainly produced through a well-established non-catalytic industrial process, the steam-cracking of alkanes, and the mixture of products is then separated by fractional distillation [48]. Catalytic dehydrogenation can relate to this, where an alkane loses hydrogen at high temperatures to produce a corresponding alkene [47]. The reverse of it will be the catalytic hydrogenation of alkenes as shown in Fig. 2.

It is noted that the application of zeolite-based catalysts in olefin technology is very relevant in refinery and chemical commodities industry at the present time [50].

Olefin is mainly used to manufacture polymers. There are basically two main types of polymers that can be synthesized [51]. The first, polyethylene, is a simple linear structure with repeating units. These fibers are used mainly for ropes, twines and utility fabrics. The second type, polypropylene, is a three-dimensional structure with a backbone of carbon atoms. Methyl groups protrude from this backbone. Stereoselective polymerization orders these methyl groups to the same spatial placement. This creates a crystalline polypropylene polymer. The fibers made with these polymers can be used in apparel, furnishing and industrial products [51].

4.1. Green olefins

There is no doubt that the world demand for olefin-based products is increasing year by year. Fig. 3 depicts ethylene

Table 1 – Basic physical and chemical properties of glycerol [8].

Properties	Values
Chemical formula	C ₃ H ₅ (OH) ₃
Molecular mass	0.0921 kg mol ⁻¹
Density	1261 kg m ⁻³
Viscosity	1.5 m ⁻¹ kg s ⁻¹
Melting point	291.35 K
Boiling point	563.15 K
Food energy	4184 J g ⁻¹
Flash point	433.15 K

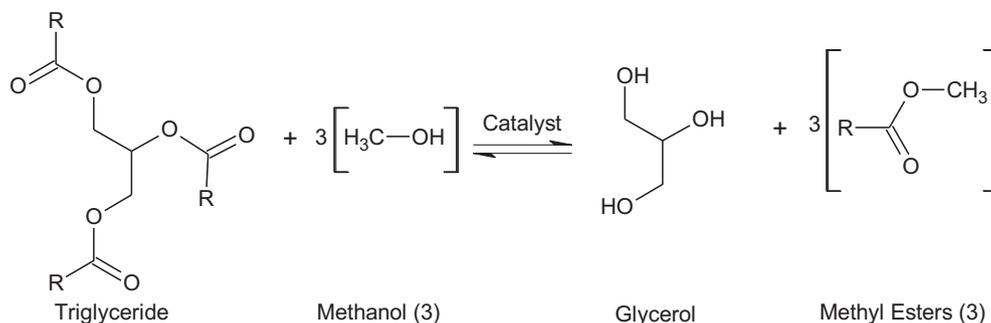


Fig. 1 – Transesterification reaction involving triglyceride and methanol to produce methyl ester and glycerol as a byproduct [10].

capacity growth trend and production from Middle East, Northeast Asia, West Europe and North America increases from year 1990 to 2011 [52]. The growth of olefin can be related to the huge world consumption since the demand is crucially high. Chemical Market Associates, Inc. (CMAI) recently compiled the World Light Olefins Analysis, an annual global study that covers the future outlook for supply, demand, production, capacity, trade, pricing and profitability of the global ethylene and propylene markets from 2003 to 2013. The outlook warns of a serious impact in the production cost of light olefins as well as the fierce competition between manufacturers [53]. An olefin plant under Lyondell Basell in Terni, Italy was shut off permanently in the first quarter of 2010 due to claims that it was no longer economically viable [54]. This was attributed to the economic turmoil, competitive battle between olefin manufacturers but most importantly the high production cost of olefins. Such high production cost of olefin is directly related to the increasing raw material cost. Thus, employing cheaper and abundant alternative such as glycerol can potentially reduce olefin production cost in the long run.

As mentioned earlier, olefins are made from naphtha, a source which is not renewable and releases green house gasses (GHG) when it is processed. Huge emission of GHG has negative attributes to the environment and can add up to the problem of global warming. Since, glycerol is abundantly available from the evolvement of biodiesel process, utilizing it as a green sustainable raw material for olefin production can be a desirable idea.

The green olefin will have premium market since it is produced from renewable material and is sustainable compared to the traditional olefin production process. Green bio-olefin like this could also be used for numerous biomaterial applications such as chiral separation media, membranes, drug delivery, proteomics and surfaces for artificial implants [55]. An example of bio-olefin green product is the first

polypropylene cup made entirely from biomass via fast pyrolysis and then (methanol to propylene) MTP[®] technology in Borealis, Norway [56]. The propylene is of polymer-grade quality and identical to the standard PP. Such scenario indicated that efforts and study are presently being geared towards developing green bio-olefin technology. On top of that green bio-olefin will perfectly complement the future development of various green technology efforts such as green car and green building.

5. Catalytic conversion of alcohol/glycerol to olefins

5.1. General overview

The catalytic conversion of glycerol to olefins is relatively a new potential process that can be further explored. Olefin was obtained as one of the byproducts along with paraffin, acetaldehyde, acetone, 2-propanol, acids, C₅ + BTX, other CHO and coke in the process of glycerol dehydration to obtain acrolein [4]. In another study, glycerol was reacted with hydrogen to produce propane. In the process, propene and hydrogen were repeatedly formed before propane was produced [5]. The olefin selectivity was observed to increase when the temperature was raised over ZSM-5 zeolite catalyst in a fixed bed reactor [4]. By controlling certain process parameters and catalyst properties olefin production can prevail through the catalytic process. Since the area on GTO is relatively new, there are very few reports or documentations related to glycerol transformation to olefins. Similarly, studies on glycerol conversion to gasoline range hydrocarbons are also lacking [57]. However, the study on oxygenates like methanol and ethanol to hydrocarbon, especially to olefin is very well established [58–66]. It all started with the accidental discovery

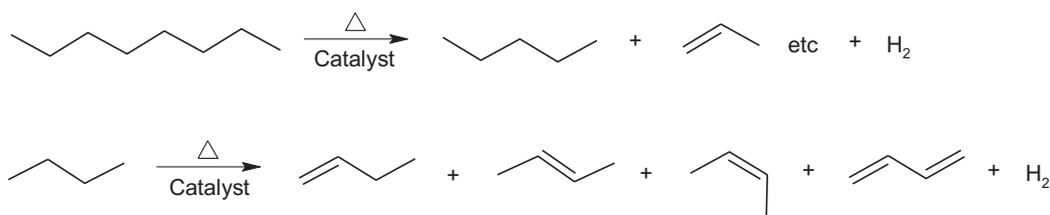


Fig. 2 – Catalytic dehydrogenation of alkane [47].

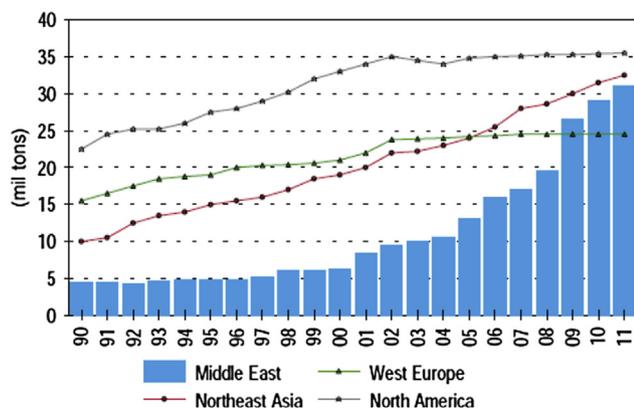


Fig. 3 – Ethylene capacity growth trend [52].

of methanol to gasoline (MTG). A group at Mobil was trying to convert methanol to other oxygen-containing compound over a ZSM-5 catalyst and end up getting hydrocarbons [67]. Another group tried to alkylate isobutene with methanol over ZSM-5 and identified a mixture of paraffins and aromatics boiling in the gasoline range which all originated from methanol [58]. Since the debut, research from alcohol-to-hydrocarbons led to investigations partially related to the transformation to olefin as well.

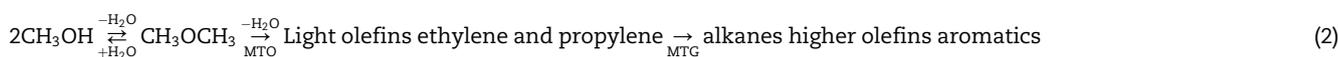
The chemistry of methanol to hydrocarbons mechanistic and kinetic considerations has been heavily discussed. More than 20 possible mechanistic proposals for the formation of first C–C bond for hydrocarbon have been reported [65,68,69]. Some of the

converted into ethylene and butene, combined in a metathesis step where bonds of both hydrocarbons are broken and rearranged into propylene. The reaction is shown in Eq. (1):



Both ethylene dimerization and metathesis are all commercially available technologies but are mostly used for application other than propylene manufacturing [76]. Nevertheless, methanol and ethanol conversion to olefins are the most established work and comprehensively researched over the last three decades [77]. Various mechanisms, processes variables, reactors, catalysts and results concerning the production of olefins from methanol and ethanol have been reported. Table 2 tabulates some of the studies.

In general, the processes highlighted in Table 2 involve a reversible dehydration process whereby water is removed from alcohol and produces very important intermediate, dimethyl ether (CH_3OCH_3). Dimethyl ether (DME) is an organic compound and also the simplest ether. It is a colourless unstable gas and it needs to be immediately reacted to produce olefin. Hence, subsequent removal of water from DME will lead to light olefin formation (MTO, methanol to olefin) as shown in Eq. (2). The light olefins can then be stored or further processed to alkanes, higher olefins and aromatics via hydrogenation and oligomerization processes. This is possible via the methane to gasoline process which employs zeolite ZSM-5 catalyst for reaction at high temperature.



mechanisms deeply discussed were the carbocationic [70,71], free radical [68], consecutive type [72], parallel type [73] and rake [74]. From all the process mechanisms mentioned, three major steps are identified in the production of olefins which are (1) formation of dimethyl ether; (2) initial C–C bond formation; (3) and subsequent conversion of the primary products hydrocarbon. The second step has enticed huge debate and triggered researchers to propose their mechanism to produce the first olefins [69]. Besides methanol, ethanol conversion to hydrocarbon has also been conducted. The gas-phase formation of ethylene and/or aromatics production from ethanol over H-mordenite and Ni/HZSM-5 catalysts has been reported [59,60]. Gayubo et al. [75] reported the successful transformation of other alcohols and oxygenates, such as, propanol, butanol, acetone, and butanone to higher paraffins and olefins over HZSM-5 catalyst. The proposed reaction scheme involved the dehydration of oxygenates to corresponding olefins and paraffins as the first step, followed by oligomerization.

5.2. Methanol and ethanol conversion to olefins

A non-straight forward step of obtaining propylene is by utilizing ethanol and butanol. The two alcohols are first

Numerous types of catalysts and reactors have been tested to produce olefins. Chang et al. [78], Givens et al. [79] and Wunder et al. [80] were among the earliest researchers to study the conversion of methanol to olefin. Chang's group worked with zeolite ZSM-5 and studied the effect of flow rate and discovered significant improvement in conversion of methanol. Givens' group on the other hand pre-screened other catalysts for the same process and found that ZSM-34 performed better than the others. Meanwhile, Wunder's group studied a different batch of catalysts at that time namely H-chabazitec, H-erionitec and ZK-5 and obtained quite impressive ethylene and propylene selectivity between 55.1 and 57.5%. In 1991, Marchi and Forment reported their work on methanol to light alkenes using SAPO molecular sieves and obtained decent amount of olefin selectivities [81]. Takahara et al. studied the dehydration of ethanol into ethylene over various solid acid catalysts and concluded that H-Mordenite (20) and H-Mordenite (90) gave the best performance. It was suggested that the ethylene was produced via an intermediate compound, diethyl ether and associated with the number of Broensted acid sites available in the catalyst [59]. Zaidi investigated methanol conversion to hydrocarbon with several modified zeolite ZSM-5 catalyst impregnated with ZnO, CuO and also CuO/ZnO. He

Table 2 – Literatures related to alcohol conversion and selectivity to olefin and hydrocarbons.

No	Process/Reactor	Process parameters	Catalysts	Conv. (%)	Selec. (%)	References	
1	Ethanol to ethylene	$W.F^{-1}$ (g cat min $mmol^{-1}$ C ₂ H ₅ OH) = 12.5 T = 162 °C, 0.1 MPa	H-Mordenite (20)	82.0	80.0	[59]	
			H-Mordenite (90)	83.0	84.0		
2	Ethanol to hydrocarbon	Temperature = 400 °C Catalyst mass = 0.2 g ⁻¹ Note: Selectivity is for ethylene & propylene only	H-Beta (Si/Al = 27)	94.8	89.7	[63]	
			HZSM-5 (Si/Al = 29)	92.2	26.3		
			HZSM-5 (Si/Al = 190)	96.4	99.3		
			USY (Si/Al = 6.3)	93.7	96.6		
			H-Mordenite (Si/Al = 18)	79.8	96.8		
3	Alcohol (methanol & ethanol) to olefin	Fix bed reactor, Ar flow: 60 mL min ⁻¹ , Mass: 4 g T = 400 °C, Quartz tube reactor 0.8 m × 0.025 m ID. Results taken for time on stream = 2nd hour	ZSM-5/SiC (E 100%)	73.0	75.0	[64]	
			ZSM-5/SiC (E:M-25:75%)	57:76	83.5		
			ZSM-5/SiC (E:M-75:25%)	58:65	50.0		
			E = Ethanol M = Methanol				
4	Methanol to olefin	T = 371 °C, P = 100 kPa, W/F ₀ (g cat h mol ⁻¹) = 0.07 0.7 70.0	HZSM-5 catalyst			[78]	
					32.6		0.16
					100.0		8.0
					100.0		1.2
5	Methanol to olefins	T = 380 °C	Offretite (7.9)	82.8	2.4	[79]	
			Erionite (9.8)	76.4	6.1		
			Zeolite T (7.2)	69.1	2.0		
			ZSM-34 (10.2)	88.2	22.4		
6	Methanol to olefins	T = 380 °C Methanol + water	Offretite (7.9)	91.8	40.4	[79]	
			Erionite (9.8)	84.8	39.3		
			Zeolite T (7.2)	33.0	20.6		
			ZSM-34 (10.2)	72.2	41.4		
7	Methanol-water to ethylene, propylene, Butane	T = 538 °C GHSV = 500 h ⁻¹ T = 370 K ^a GHSV = 1.3 h ⁻¹ ^b GHSV = 1.0 h ⁻¹	H-chabazite	100.0	57.0	[80]	
			H-erionite	100.0	55.1		
			ZK-5	100.0	57.5		
			H-chabazite ^a	3.0	63.0		
			H-erionite ^a	5.0	85.0		
8	Methanol to olefin	T = 480 °C P = 100 kPa	SAPO-34 (0.15)	99.9	40.1	[81]	
			SAPO-34 (0.15)	99.9	40.6		
			SAPO-34 (0.15)	99.9	39.9		
			SAPO-34 (0.05)	99.9	40.7		
			SAPO-34 (0.05)	96.7	33.9		
9	Methanol to hydrocarbon	W/F_{AO} (g cat h mol ⁻¹ methanol feed) = 4.138 Temp = 300 °C Pressure = 100 kPa	HZSM-5 (Si/Al = 45)	38.0	15.2	[82]	
			ZnO/HZSM-5	60.0	22.5		
			CuO/HZSM-5	97.0	42.2		
			CuO/ZnO/HZSM-5	95.0	41.1		
10	Methanol to olefin	T = 320 °C WHSV = 4–30 h ⁻¹ ^c Ethylene and propylene only	ZSM-5-coated ceramic foams (Si/Al = 32); Pellets	65.0	35.0 ^c	[83]	
			Foamcoat; 18 μm	66.0	42.0 ^c		
			Foamcoat; 5 μm	67.0	43.0 ^c		
11	Methanol to olefin	Monolith reactor. Results taken for time on stream = 2nd hour	ZSM-5/SiC double layer	90.0	65.0	[84]	
			ZSM-5/SiC single layer	76.0	64.0		
			ZSM-5 powder	71.0	31.0		
12	Methanol to olefin	T = 350 °C WHSV = 0.70 h ⁻¹ 100 min of time stream ^d Yield of olefin	MOR (5)	52.1	52.1 ^d	[85]	
			MOR (12)	92.4	92.4 ^d		
			MOR (55)	90.7	80.7 ^d		
			MOR (103)	94.1	94.1 ^d		

a GHSV = 1.3 h⁻¹b GHSV = 1.0 h⁻¹

c Ethylene and propylene only

d Yield of olefin

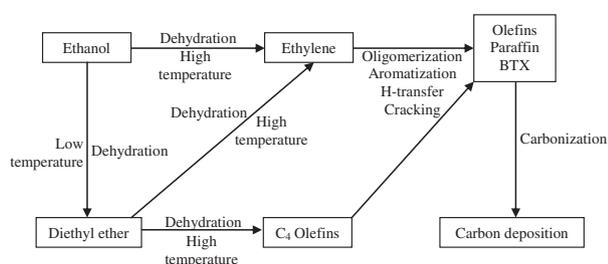


Fig. 4 – Supposed reaction pathway from ethanol to olefin [63].

discovered that CuO/ZSM-5 produced highest methanol conversion (97.0%) and highest hydrocarbon selectivity (42.2%) compared to other catalysts at 400 °C and 100 kPa [82]. Inaba et al. [63] carried out the conversion of ethanol to olefin using H-Beta, HZSM-5, USY and H-Mordenite and obtained very encouraging ethanol conversion and light olefin selectivity. The supposed reaction pathway proposed by Inaba et al. is shown in Fig. 4. In this process, ethylene is obtained via two processes; direct dehydration of ethanol; and dehydration of DME; both taking place at high temperature in presence of catalyst. Higher molecular weight olefin can be further obtained via oligomerization, aromatization, H-transfer and cracking of the lighter olefins.

Most of the research described previously utilized fixed bed reactors. However, Patcas [83] adopted ZSM-5-coated ceramic reactors while Ivanova et al. [84] integrated ZSM-5 with monolith reactor for the process of methanol conversion to olefin. Both reactors showed encouraging outputs when using the same common catalyst. Interestingly, Ivanova et al. [64] continued their investigations to see the effects of mixing methanol and ethanol to produce olefins in the monolith reactors. They proposed that the use of ZSM-5 coated on B-Sic foam packings in the alcohol-to-olefins reaction improved activity/selectivity substantially when compared to conventional catalyst in the form of powder or extrudates. In a more recent investigation, the effect of acid sites density of MOR zeolite towards the olefin selectivity as well as its deactivation was investigated [85]. Regardless of the acid density, the MOR zeolites gave high conversion and high lower olefin yields at the initial rate of the MTO reaction. In addition, it was also reported that the conversion and yield of the lower olefins decreased in the order of decreasing Si/Al ratios of the MOR zeolite.

From the transformation of methanol to olefin, the steam stability of the HZSM-5 type zeolites is greatly improved by

adding alkaline earth metals [86]. The high selectivities to light olefins are attained at high temperature over highly siliceous zeolites. It was also reported that high selectivity to light olefins was obtained in the methanol conversion over HZSM-5 type zeolites containing alkaline earth metals, especially calcium [86]. Their results have possibly helped to narrow down the choice for catalysts to be tested for the conversion of glycerol to olefins.

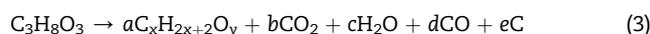
The characteristics of alkaline earth metals modified HZSM-5 zeolites in Table 3 indicated the prepared HZSM-5 type zeolites containing alkaline earth metals (M-HZSM-5) had a well-defined HZSM-5 type structure deemed suitable for the transformation of glycerol to olefins.

It has been shown that alcohol, in the context of methanol and ethanol, can be converted to olefin crucially made possible with the existence of active catalyst which dehydrated the glycerol to produce DME and subsequently light olefins. With such theoretical comprehension, the knowledge can be helpful in understanding glycerol conversion to olefin, albeit more complicated.

6. Glycerol transformation to olefins (GTO)

6.1. Glycerol as a potential source for olefin production

Glycerol transformation to olefin is a new and not yet an established study area. In view of that, several routes to obtain hydrocarbons from glycerol have been studied. It is vital to understand the real problem concerning glycerol conversion. The biggest challenge with glycerol conversion is how to efficiently remove oxygen from the hydrophilic properties and convert it into a hydrophobic molecule with appropriate combustion capabilities by increasing the hydrogen ratio in the hydrocarbon product. Oxygen can be removed from glycerol as CO, CO₂ or H₂O through the reaction in Eq. (3) [87].



An effective hydrogen-to-carbon ratio (H/C_{eff}) as defined in Eq. (4), was proposed to comprehend the chemistry involved in the conversion of biomass-derived oxygenates such as glycerol [88]. The H/C_{eff} ratio of biomass-derived oxygenates is lower than that of petroleum-derived feedstocks due to the higher oxygen content of biomass-derived molecules. The H/C_{eff} ratio of carbohydrates glycerol is 2/3. The H/C_{eff} ratio of petroleum-derived feeds ranges from ~2 for highly paraffinic feeds to slightly >1 for highly aromatic residues. In this respect, glycerol is a hydrogen-deficient molecule compared to petroleum-based feedstocks.

$$H/C_{eff} = \frac{H - 2O - 3N - 2S}{C} \quad (4)$$

where H, C, O, N, and S are the moles of hydrogen, carbon, oxygen, nitrogen, and sulfur respectively.

Zhang et al. [89] recently investigated the effect of H/C_{eff} on ten types of biomass-derived feedstock including glycerol for obtaining olefins/aromatics using zeolite ZSM-5. They concluded that the higher the H/C_{eff} ratio, the higher the

Table 3 – Characteristics of HZSM-5 zeolites containing alkaline earth metals [86].

Zeolite	Atomic Ratios		BET surface area (m ² g ⁻¹)
	Si/Al	Alkaline earth metal Al ⁻¹	
HZSM-5	120		342
Mg-HZSM-5	94	0.89	336
Ca-HZSM-5	117	1.63	341
Sr-HZSM-5	93	1.29	301
Ba-HZSM-5	90	1.35	301

Table 4 – Literatures covering the improvement/process of glycerol conversion to olefins.

No	Process/Reactor	Process parameters	Catalysts	Conv. (%)	Selec. (%)	References
1	Glycerol to olefin	GHSV = 105 h ⁻¹ , fixed bed reactor, Temperature = 650 °C.	CuZSM-5	100.0	16.28 (% yield)	[2]
2	Glycerol to propane synfuel	LHSV = 0.65 h ⁻¹ , Trickle bed reactor, 98% pure glycerol, H ₂ supplied = 15.168 MPa, T = 343 °C	Macro-pore nickel–tungsten catalyst	100.0	26.6	[3]
3	Glycerol to olefin	Tester/Temp/Catalyst to feed ratio/Resid. time (s)/WHSV (h ⁻¹): MD/500 °C/12/0.7/396 MD/650 °C/51/0.7/108 MD/500 °C/11/0.7/431 MD/500 °C/48/1.4/55 MD/650 °C/45/0.7/121 MAT/700 °C/4/30/30 MAT/720 °C/6/83/7 Glycerol–water: 50% MD: Microdowner reactor MAT: Microactivity test reactor	USY USY ZSM-5 ZSM-5 ZSM-5 ZSM-5 USY	100.0 100.0 100.0 100.0 100.0 100.0	8.4 19.4 9.2 18.4 26.3 32.2 19.4	[4]
4	Glycerol to ethane and propane	5 wt.% Pt/support 1.0 g, Glycerol 16.4 mmol, H ₂ O 500 mmol, T = 270 °C, 12 h, H ₂ /N ₂ = 85/15 (vol.%), 2.0 MPa (room temp.). Pretreatment: calcination at 500 °C for 5 h, and reduction at 200 °C and 2 MPa of hydrogen for 4 h.	HZSM-5 (29) HZSM-5 (29) H-MOR (18.3) γ-Al ₂ O ₃ USY (6.3) Beta (27) SiO ₂ HZSM-5 (29) γ-Al ₂ O ₃	80.2 35.7 79.6 77.4 47.3 12.1 5.13 70.7 79.6	59.5 58.65 52.9 22.35 52.8 44.2 23.1 55.3 59.4	[5]
5	Glycerol to fuel	Single catalytic bed W/F = 0.5 h ⁻¹ Temp = 300–400 °C	HZSM-5 689.47 kPa 2068.43 kPa	91.0 95.0	18.0 19.0	[15]
6	Glycerol to Olefin	50% glycerol–water mixture T = 500 °C TOS = 30 s ^a Ethylene yield	FCC1 ECat ZSM-5 Al ₂ O ₃ Y-zeolite	98.0 83.0 87.0 77.0 100.0	5.2 ^a 3.0 ^a 13.0 ^a 2.5 ^a 6.0 ^a	[87]

a Ethylene yield

selectivity towards olefins and aromatics, and the less coking takes place. It is thus imperative to shift glycerol towards higher H/C_{eff} ratio.

One way to increase the H/C_{eff} ratio is with fluid catalytic cracking (FCC) process. The process is very effective at removing oxygen from glycerol; however, oxygen is not released via the optimal pathway. The process is also able to produce hydrogen through steam-reforming reactions or by direct dehydrogenation of the carbohydrates and hydrocarbons, the water-gas-shift (WGS) reaction, and decarbonylation of partially dehydrated species or the feedstock. The occurrence of these reactions will be consistent with the formation of CO, CO₂, graphitic coke, and H₂ that have been observed experimentally [87]. On the other hand, the H₂ produced in these reactions can be consumed in reactions that increase the H/C_{eff} ratio of the products, leading to olefins and alkanes. Hydrogen will be exchanged through hydrogen-transfer reactions between two hydrocarbon/carbohydrate chains or through consecutive dehydrogenation/hydrogenation reactions. The hydrocarbons formed through these first reaction steps will then undergo the traditional oligomerization cracking chemistry of hydrocarbons [87].

6.2. Recent glycerol to olefin-related studies

It can be stipulated that selective production of olefins and aromatics requires a proper balancing of dehydration, hydrogen-producing, and hydrogen-transfer reactions by selecting the appropriate catalyst and reaction conditions [87]. During the catalytic cracking of glycerol, dehydration reactions occur on acid sites, producing water and dehydrated compounds [2,5,9].

Steam reforming of dehydrated species produces CO and H₂. The WGS reaction can produce more H₂, and increasing the partial pressure of water increases the rate of the WGS reaction. The dehydrated species can react with the hydrogen via hydrogen-transfer reactions to produce olefins and aromatics. Decarbonylation reactions also may occur and will produce ethylene and CO from acrolein. Larger aromatic and olefin compounds are probably formed by Diels–Alder and aldol condensation reactions of olefins and aldehydes [87].

Besides the glycerol conversion process mentioned above, the production of liquid fuels via catalytic glycerol processing coupled with Fischer–Tropsch synthesis has also been pursued [90]. In this study, glycerol was directly converted to

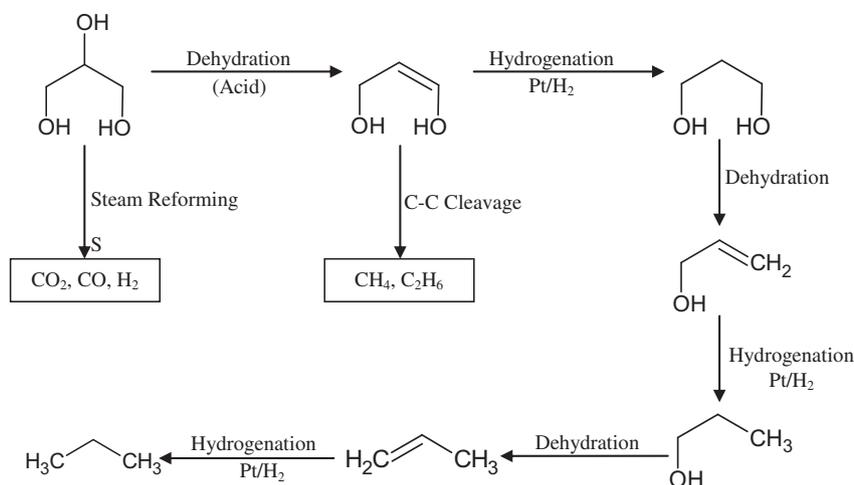


Fig. 7 – Postulated scheme for gaseous products formation from glycerol in the presence of hydrogen over Pt/HZSM-5 catalyst [5].

liquid alkanes via an integrated process involving catalytic conversion of concentrated glycerol solutions to H_2/CO gas mixtures (synthesis gas) combined with subsequent Fischer–Tropsch synthesis. The addition of Re to C-supported Pt-based catalysts increases the rate of synthesis gas production by an order of magnitude at conditions leading to higher CO pressures. Also, the Pt–Re/C catalyst produces synthesis gas at high rates and selectivities suitable for Fischer–Tropsch synthesis (H_2/CO ratios between 1.0 and 1.6) from concentrated glycerol feed solutions (between 50 and 80%) at low temperatures (548 K) and moderate pressures (0.5–1.7 MPa). Notably, the water and oxygenated hydrocarbon byproducts from glycerol conversion (e.g. acetone, and ethanol, acetol) either have negligible effects on the subsequent Fischer–Tropsch synthesis or have synergistic effects by participating in hydrocarbon chain growth [90].

Liquid hydrocarbons can be also produced from glycerol in a two-bed, single reactor system at 548 K and pressures between 0.5 and 1.7 MPa. The hydrocarbon products have a selectivity to C_5^+ alkanes of 75% at 1.7 MPa, and the aqueous liquid effluent contains between 5 wt% and 15 wt% methanol, ethanol, and acetone, which can be separated from the water via distillation and used as chemicals or recycled for conversion to gaseous products [90]. The study by Simonetti et al. [90] proved what have been claimed by Soares et al. [38] that liquid hydrocarbons can be obtained from glycerol. Fig. 5 illustrates the schematic of liquid fuel and chemical production via catalytic processing of aqueous glycerol. Syngas can be

produced from glycerol and hence consecutively yields liquid hydrocarbons, methanol and other important chemicals via Fischer–Tropsch synthesis. Without doubt, the integrated process has the potential for improving the economics of liquid fuel production from biomass via Fischer–Tropsch synthesis. However, in order to obtain olefins hydro-cracking of liquid fuel is still needed – a very costly process to consider.

Table 4 lists the literatures associated with the transformation of glycerol to olefins. Corma et al. [87] have earlier reported the formation of olefins from glycerol water mixture of 50% using FCC, ECat, ZSM-5, Al_2O_3 and Y-zeolite catalysts at temperature 500 °C. The following year, using micro-downer (MD) and microactivity test (MAT) reactor, Corma et al. [4] tested the performance of ZSM-5 and USY with temperatures ranging from 500 to 700 °C. They have found that with increasing reaction temperature, the yields of CO, CO_2 and light olefins, methane and C_5^+ hydrocarbons increased. On the other hand, the formation of other major products such as oxygenates and coke decreased. It was

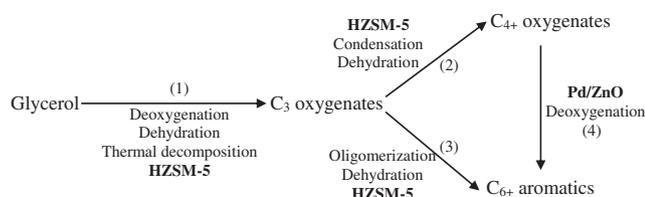


Fig. 8 – Glycerol conversion pathways proposed by Hoang et al. [15].

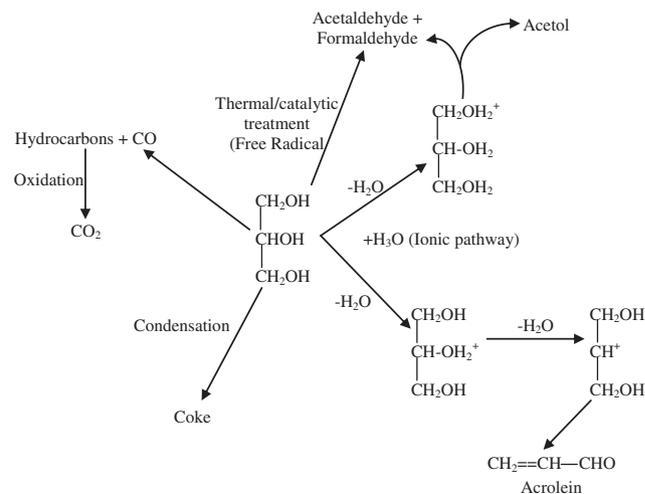


Fig. 9 – Proposed reaction pathways for catalytic conversion of glycerol [9].

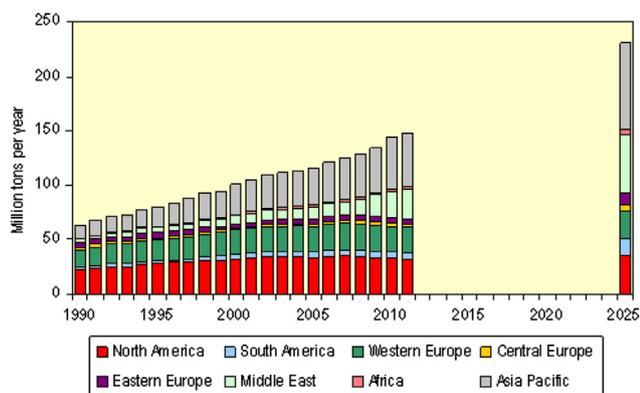
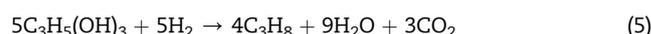


Fig. 10 – Ethylene capacity development [93].

found that ZSM-5 catalyst performed comparatively far better than the other catalysts. These findings indicated that high reaction temperatures ($\sim 500\text{--}700\text{ }^{\circ}\text{C}$) and low space velocity is ideal for light olefin production. The light olefin production was highest at $700\text{ }^{\circ}\text{C}$, catalyst to feed ratio 4, residence time 30 s and WHSV 30 h^{-1} . The overall schematic glycerol conversion is shown in Fig. 6. The MD unit operated at catalyst residence time closed to 1 s and catalyst to feed (CTF) ratios of 12–51 to simulate adiabatic mixing of the glycerol solution ($100\text{ }^{\circ}\text{C}$) and the catalyst (close to $700\text{ }^{\circ}\text{C}$ from an industrial regenerator).

In a separate study conducted by Murata et al. [5], glycerol–water mixture and hydrogen were converted to propane over several catalysts including Pt–ZSM-5. In the process, dehydration and hydrogenation repeatedly took

place and propylene was formed as intermediate (Fig. 7). Through bifunctional reaction pathway, direct steam-reforming process also took place and resulted in the formation of CO , CO_2 and H_2 . Pt/HZSM-5 was proven to be the best with conversions up to 80.2% and C_3H_8 selectivity of 35.4% without any trace of coke formed. According to them, glycerol dehydrated over the active sites of HZSM-5 to give unsaturated glycol or aldehyde species, which migrated to Pt sites where they underwent hydrogenation to form saturated glycol. Formations of methane and ethane took place by cleavage of C–C bonds of the above intermediate species as compared to hydrogenation of dehydrated reaction cycles. Deep reforming of C_3 intermediates, as well as glycerol and water-gas-shift reaction produced CO_2 and CO . Thus, propane formation from glycerol may be explained in terms of cooperative effects on Pt and HZSM-5. The catalyst was found to be active for reforming of glycerol as indicated by the NH_3 -TPD analysis. Adding hydrogen accelerated the hydrogenation of olefinic intermediates to propane. The general equation for the formation of propane from glycerol is shown in Eq. (5).



Hoang et al. [15] studied the catalytic conversion of glycerol to fuels using HZSM-5 catalyst via a combination of deoxygenation, dehydration and thermal decomposition of glycerol–water mixture. The process involved pressure of 0.76 and 2.1 MPa and temperature $300\text{--}400\text{ }^{\circ}\text{C}$ to produce C_3 oxygenates which included propylene before fuel was formed using HZSM-5 and Pd/ZnO catalysts. The proposed reaction scheme by Hoang et al. is illustrated in Fig. 8. Recently, the same group

Table 5 – Comparison of technologies to obtain olefin.

Technology	Feedstock	Feedstock cost, $\text{\$ tonne}^{-1}$	Process	Catalysts	State of Development	References
Naphtha to olefins	Non-renewable, secondary product	600–860 [96]	Cracking, dehydrogenation	Zeolite-based catalyst	Industrial plant	[94,95]
Methanol to olefin (MTO)	Non-renewable, secondary product	310–420 [101]	Dehydration, demethanizer, depropanizer, deethanizer, CO_2 removal	Silicoaluminophosphate, SAPO-34	Industrial plant	[97,98]
Ethanol to olefin (ETO)	Non-renewable, secondary product	720–850 [100]	Dehydration	Syndol	Pilot plant	[99]
Methane to olefins	Non-renewable, secondary product	395–397 GJ^c [104,105]	Oxidative chlorination	Lanthanum trichloride	Pilot plant	[102]
Coal to olefin (CTO)	Non-renewable, primary product	65–300 [108,109]	Coal to syngas to DME	SAPO molecular sieve	Industrial plant	[107]
Glycerol to olefin (GTO)	Renewable, byproduct from biodiesel	500–520 ^a 130–170 ^b [111,112]	Dehydration, dehydrogenation	Zeolite ZSM-5 based catalyst	Laboratory	[2,4]

a Refined.

b Crude.

c Based on natural gas price in September 2010 (measured in GJ).

varied the W/F of zeolite HZSM-5 catalyst and glycerol feed; and deduced as W/F increased, olefin gaseous increased up to almost 40% when employing W/F = 8. The operating temperature was 400 °C at atmospheric pressure. The olefin gaseous comprised mainly of propylene and traces of ethylene [57].

The etherification of glycerol with isobutene to monoethers, diethers and triethers using Amberlyst 35 wet ion exchange resin was studied by Karinen and Krause [41] and it was found that if isobutene was in excess, isobutene oligomerization reaction forming olefin (mainly C₃) would take place. However, proper control of the reacting parameters was required including the molar ratio of glycerol/isobutene and temperature. Etherification of acid-catalyzed glycerol with isobutylene over mesostructured silicas yielded the valuable tert-butylated derivatives mostly used for reducing the emission of particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes [91].

Lu et al. [92] studied the effect of addition of metal on zeolite structure to produce olefins. The Cr/HZSM-5 catalysts with trace amount of Cr were initially used for catalytic cracking of isobutane. The results suggested that when the loading of Cr in the Cr/HZSM-5 catalysts was less than 0.038 mmol g⁻¹ Cr, especially at Cr loading of 0.004 mmol g⁻¹, both the reactivity of isobutane (cracking) and the selectivity to light olefins of Cr/HZSM-5 samples were greatly enhanced compared with the unpromoted HZSM-5, and very high yields of olefins (C₂ + C₃) and ethylene were obtained. The yield of olefins (C₂ + C₃) and ethylene reached 56.1% and 30.8%, respectively, at 625 °C when 0.004 mmol g⁻¹ Cr was loaded on HZSM-5 sample.

Pathak et al. [9] in their quest to optimize glycerol conversion to liquid fuel using HZSM-5, HY, silica-alumina and γ -alumina catalysts proposed reaction pathways for the process as shown in Fig. 9. They concluded that the acidity of the catalyst had major effect on the glycerol conversion, liquid product yield and acetaldehyde, acrolein, formaldehyde and acetol yields. Nevertheless, hydrocarbon was formed in an unknown quantity and could have contained olefins. Although HZSM-5 in this case has the highest acidity compared to the other catalysts, the glycerol conversion was not at its maximum. It was because during cracking glycerol molecules were adsorbed on the catalyst surface. The products were not easily desorbed from relatively strong acid sites and gave lower glycerol conversion over HZSM-5. This could be attributed to significant pore diffusional limitations which reduced the effectiveness of the reaction rate. It was also discovered that the liquid product yield decreased significantly when the total acidity was increased. As liquid product yield was a function of glycerol conversion, the decrease in glycerol conversion led to lower liquid product yield at higher acidity. This effect however, has unknown influence to olefin formation and more related studies need to be carried out.

Recently, catalyst screening for glycerol conversion to light olefin reported yield of 16.28% over CuZSM-5 [2]. TPD analysis suggested that strong acid sites on the catalyst surface triggered initial glycerol dehydration and dehydrogenation rates. This proves that GTO has great potential to yield light olefin and further investigation is required to improve both the process and catalyst.

7. Future perspectives

The demand for olefins is speculated to continue to rise in future. In the actual scenario, olefin consumption forecasts reflect a subsequent marginal recovery in 2010 after suffering a downturn of unprecedented severity in the previous year due to bad economics, logistic, operational and regional factors [93]. This is then followed by a period of strong economic recovery up to a peak in 2025 as illustrated in Fig. 10.

Since olefin is such an important chemical, various technologies for the production of it from other sources are currently being pursued. Traditionally, olefins are obtained from hydro-cracking of naphtha [94,95] which is quite costly due to exorbitant raw material costs [96]. In addition, there are other chemical processes that are cooperatively used to produce olefins such as elimination reactions, synthesis from carbonyl compounds, olefin metathesis and coupling reactions but all of them still very much depend on petroleum as the main raw material [95].

The most widely used methods for producing olefins from methane proceed via methanol-to-olefins or Fischer-Tropsch process [97] with synthesis gas as intermediate products. Both processes are capital and -intensive energy-intensive [98]. The ethanol to olefin technology has also been commercialized by Chematur Engineering Group from Sweden [99]. The process utilizes Syndol based catalysts to react with ethanol in order to obtain olefin. Less is known about the actual costing of this process. However, from Table 5, it is obvious that ethanol price [100] is double the price of methanol [101]. It can be deduced that the utilization of ethanol as feedstock to produce olefin may not be economically attractive. Furthermore, both methanol and ethanol are valuable chemicals, and therefore using it as a feedstock maybe futile.

Researchers from Dow Chemicals have found new ways to produce olefins from underutilized methane via a process called oxidative chlorination [102] where methane reacted with hydrogen chloride over lanthanum trichloride (LaCl₃) catalyst. The resulting methyl chloride can then be converted into either chemicals or fuel using well-known chemistry [103]. Although it is a good process, the fact that methane from natural gas is not renewable undermined the practicality. Nevertheless, the utilization of methane as olefins is a promising option as the feedstock is cheaper [104,105] and cleaner.

Besides obtaining olefin from naphtha from readily available process, China has established several coal-to-olefin (CTO) plants due to be commissioned at the end of 2010 [106]. CTO is seen as an answer to the world olefin supply in the near future since the technology is technologically sound [107] and coal price is very cheap [108,109]. Despite employing non-renewable feed source, the project received massive support from the government and international partners as it is projected to supplying olefin for the next 75 years, based on the present coal reserve in China [110]. In spite of exporting the coal to certain countries that prefer this commodity as a source of electricity, China coal reserves remain. Coal competition for many reasons can be a stigma, hence, there is serious need to explore ways of producing olefins from renewable sources.

Glycerol conversion to olefin can be the answer for sustainable olefin supply since glycerol is categorized as a

renewable source. In spite of higher refined glycerol price [111,112] compared to methanol and coal, there is still future for glycerol as feedstock due to the development of third generation biofuel which employs algae as a source for producing biodiesel massively [113–116]. Recently, Exxon Mobil Corporation declares that they will be testing the commercial viability of algae biofuel as an alternative energy source to supplement oil and natural gas [117]. The progress of biodiesel production from algae is astonishing and can possibly repeat the successful trend of the first generation biofuel. The earlier second generation biofuel as in *Jatropha curcas* [118], waste frying oil [17] and fatty acid distillate [119] has potential to be further developed and cannot be ignored. Both second and third generation biofuel triumphs will ensure continuous glycerol supply.

7.1. GTO research directions

In spite continuous glycerol supply, there are several issues that arise. There is a need to investigate for the most effective GTO process. Previous preliminary investigations signified two major routes.

The first one is glycerol conversion to olefin via syngas, similar to the one already commercially commissioned in China for the MTO process [120]. The main challenge in this method is to obtain optimum H_2 and CO from glycerol catalytic process. The work performed by Simonetti et al. is still in the lab scale stage [90]. Other researchers are also urged to investigate and explore this route. Once this is successfully attained in pilot plant scale, the established syngas to olefin technology will easily follow suit.

The second route is the direct catalytic glycerol transformation to olefins. This study is still at its infant stage but has potential to be further explored. More efforts should be geared towards dedicated direct GTO research. Up to this moment, what have been reported were mostly glycerol transformation to other valuable products and in the process minimum olefin was obtained [4,5]. This is proven by several report findings as tabulated in Table 4. Recently, direct GTO investigation has been reported [2]. The research outcomes pointed out that direct GTO is technologically feasible but hindered by several challenges; mostly by catalyst coking and regeneration.

Nevertheless, both routes demand more attention for the production of future sustainable and green olefins. Catalytic reactor processing and scaling up investigations need to be beefed-up. A solid heterogeneous catalyst for these processes integrated with continuous processing technology is expected to gain wider acceptance in the future due to its potential effectiveness and efficiency. While there are potential benefits that the solid heterogeneous catalyst can offer, issues related to the low catalytic activity, leachates, reusability and regeneration should be addressed and emphasized in the future research in order to ensure sustainability of the process. The reaction kinetics and also thermodynamic feasibility of GTO need to be investigated as well.

Finally, to ensure lowest production cost of GTO process, researchers should also simultaneously investigate the process using crude glycerol since it is relatively far cheaper than the refined glycerol. At an average cost of 150 \$ tonne⁻¹, crude glycerol is 360 \$ tonne⁻¹ cheaper than refined glycerol.

Nevertheless, processing crude glycerol will be very challenging since it involves the existence of water, sodium hydroxide and other impurities [121]. Hence, understanding the variation of impurities in raw glycerol and developing an appropriate GTO process that can suit this problem will be a massive contribution. Other associated matters for the production of green olefin such as logistic, economic analysis and pilot study will soon emerged alongside with the technological investigation.

8. Conclusions

Conversion of glycerol to hydrocarbons specifically olefins is still in progress and new concepts are being developed to enhance knowledge on this subject. Investigations previously carried over the past three decades involving MTHC and ETHC enhanced understanding and provided clues on how to pursue the study of glycerol to olefins. Zeolite-based catalyst such as ZSM-5, USY, mordenite, offretite, erionite, SAPO-34 and chabazite, were among those used in the process and each of them produced olefins. In most cases, fixed bed reactor was the most popular choice mainly because of its simplicity. However, investigation using ceramic and monolith reactor has also been carried out and displayed encouraging results.

Earlier findings have proven that glycerol has the potential to be catalytically converted to olefins. In these studies, catalyst plays an important role in producing olefins via a combination of cracking, steam reforming, dehydrogenation and hydrogenation process. Various catalytic systems have been tested to enhance the production of olefins in term of oxygenate content, operating temperature, space velocity and feed dilution. Almost all catalytic applications involved zeolites such as ZSM-5 and USY due to their specific porosity and acidic properties. As it was possible to obtain olefins from glycerol, several reaction schemes were postulated. However, modeling or simulation of proposed reaction schemes has been scarce. Thus, besides experimentally tweaking, testing and optimizing the process, it is essential to study the modeling and simulation aspect of it too.

Taking into consideration of the above, more investigations need to be carried out for improvement in the area of reaction and catalysis engineering, reactor development, reaction kinetics, process optimization, scaling up and pilot plant development. The tensions in the olefins/polyolefins market worldwide as well as the emerging coal-to-olefins technology developed by China, which still employ non-renewable sources, have amplified more needs to establish new renewable routes of obtaining green and sustainable olefins. Hence, the GTO is seen to be a more sustainable and environmentally friendly process. Therefore, concerted research efforts should be aggressively geared towards it.

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List of symbols

BTX: benzene
 CHO: carbon
 CTF: catalyst to feed
 CTO: coal-to-olefin
 DME: dimethyl ether
 ECat: equilibrated FCC catalyst
 ETHC: ethanol to hydrocarbon
 ETO: ethanol to olefin
 FCC: fluid catalytic cracking
 GHG: green house gas
 GHSV: gas hourly space velocity
 GTO: glycerol to olefin
 H/C_{eff} : effective hydrogen-to-carbon ratio
 LHSV: liquid hourly space velocity
 MAT: microactivity test
 MD: microdowner reactor
 MTG: methanol to gasoline
 MTHC: methanol to hydrocarbon
 MTO: methanol to olefin

P: pressure

T: temperature

TOS: time on stream

W/F: mass of catalyst per mass of feed

W/F_{AO} : mass catalysts in gram per feed of reactant

WGS: water-gas-shift

WHSV: weight hourly space velocity

ZSM-5: zeolite socony mobile 5