

Catalytic Co-Conversion of Glycerol and Proton-Donor Species to Gasoline-Range

Aromatics over Alumina

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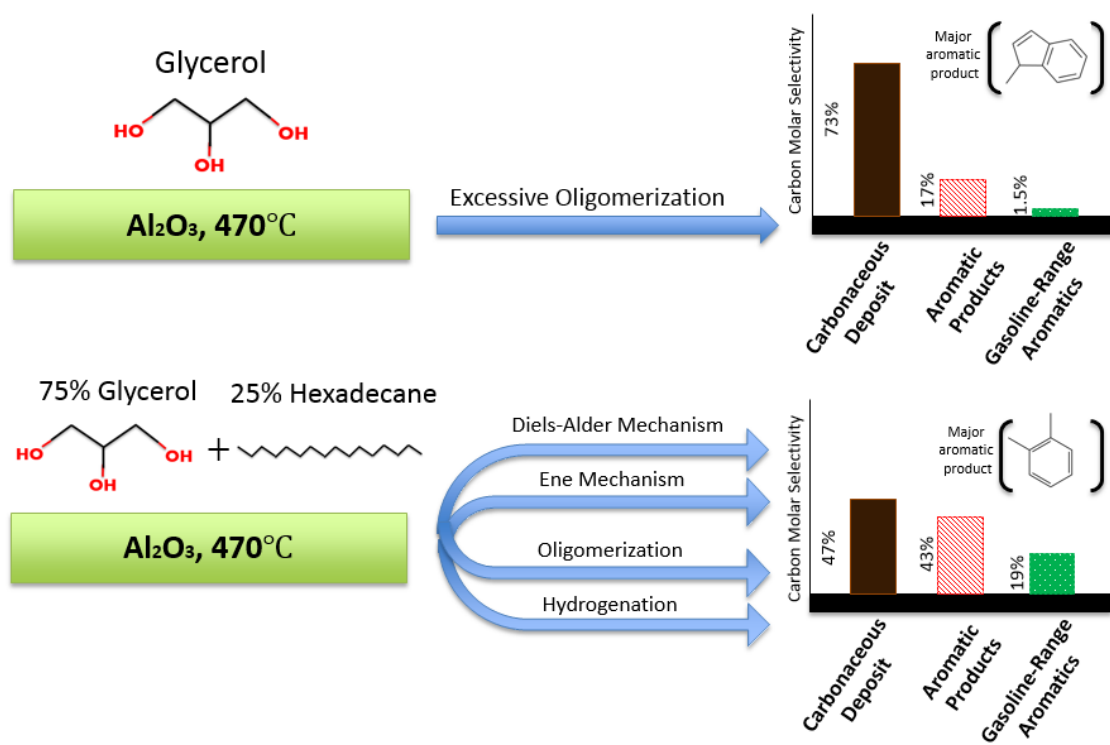
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Graphical Abstract



Abstract

Glycerol is the main by-product of the biodiesel production process. Saturation of this by-product in the market would negatively affect the growth of biodiesel production industry. Due to complexities in the purification processes of crude-glycerol, less costly chemical conversion of glycerol to value-added products and feedstocks such as propenal and aromatics has gained more attention recently. In this work, the influence of co-feeding proton-donor and olefin-donor species on the catalytic conversion of glycerol over alumina

catalyst to gasoline-range aromatics is studied. During the individual catalytic conversion of glycerol over alumina, because of the shortage of proton-donor intermediates in the process and high activity of glycerol on alumina at 470°C, glycerol mostly leads to form high carbon deposit content and aqueous phase stream, but less liquid organic production. Introducing methanol and ethanol as compound models of alcohols, and dodecane and hexadecane as compound models of long-chain alkanes next to glycerol remarkably decreases the formation of undesired stream, while selectivity to aromatics substantially increases. In terms of liquid aromatics generation and restricting the excessive carbonization on the catalyst surface, co-feeding 25 wt.% hexadecane with 75 wt.% glycerol has the highest efficiency among the selected compound models; with increasing the liquid aromatics selectivity from 17.7% to 42.5%. Additionally, Co-processing the latter compound model, noticeably shifts the distribution of produced aromatics from heavy undesired aromatics range to the gasoline-range aromatics such as xylenes and toluene. The potential influence of hexadecane on the glycerol to aromatics reaction pathway over alumina catalyst is also proposed, and the effective reactions between glycerol and hexadecane intermediates are discussed. It is also found that selecting a very high or low operational temperature would inversely affect the optimization of aromatics formation through the co-processing runs of glycerol and hexadecane.

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Table of Contents

Graphical Abstract	ii
Acknowledgement	iv
Table of Contents	v
List of Tables	viii
List of Figures	ix
List of Abbreviations	xi
Nomenclature	xii
Chapter 1- Introduction.....	1
1.1 Disadvantages of Dependence on Fossil Fuels	1
1.2 Biofuel, Alternative Source of Energy.....	4
1.3 Biofuel Production Processes	5
1.3.1 Biodiesel Production Process.....	6
1.3.2 Glycerol.....	9
1.4 Research Objectives.....	11
Chapter 2- Literature Review.....	14
2.1 Catalytic Conversion of Oxygenated Compounds to Olefins and Aromatics	14
2.1.1 Impact of Oxygenated Compound Structure on Selectivity to Olefins and Aromatics	15
2.1.2 Impact of Catalyst Characteristics on Selectivity to Olefins and Aromatics...	16
2.1.3 Impact of Reaction Condition on Selectivity to Olefins and Aromatics	18
2.2 Catalytic Conversion of Glycerol to Olefins and Aromatics	20
2.2.1 Catalytic Conversion of Glycerol over Bronsted Acid-Rich Zeolites	20
2.2.2 Catalytic Conversion of Glycerol over Lewis Acid Catalysts	24
2.3 Innovative Methods to Improve the Selectivity of Gasoline-Range Aromatics from Glycerol Catalytic Conversion Reactions.....	28

2.3.1 The Promotion of the Dehydrogenation Metal on HZSM-5.....	28
2.3.2 Two-Bed Configuration of Pd/Zno and HZSM-5 Catalysts	30
2.3.3 Catalytic Conversion of Glycerol/Alcohol Mixture	32
2.4 Gasoline-Range Aromatics	34
Chapter 3 Methods and Analytical Procedures.....	35
3.1 Experiment Sets	35
3.2 Feed.....	36
3.2.1 Glycerol.....	36
3.2.2 Methanol	37
3.2.3 Ethanol	37
3.2.3 Dodecane.....	37
3.2.3 Hexadecane	37
3.3 Catalyst Preparation and Characterization.....	37
3.4 Experimental Procedure.....	39
3.3 Product Analysis	40
3.3.1 Gas Products	40
3.3.2 Liquid Products	41
3.3.3 Solid Product.....	43
3.4 Calculation Procedure.....	43
Chapter 4- Co-processing Glycerol and Proton-Donor Species to Gasoline-Range Aromatics over Alumina.....	45
4.1 Scope of Work	45
4.2 Catalytic Conversion of Glycerol over Alumina	45
4.2.1 Mass Analyses	45
4.2.2 Product Distribution.....	46
4.2.3 Distribution of formed Aromatic products	47
4.2.4 General Overview of Glycerol Catalytic Conversion over Alumina.....	48
4.3 Co-Catalytic Conversion of Glycerol and Alcohols over Alumina	50
4.3.1 Mass Analysis	50
4.3.2 Product Distribution.....	51
4.3.3 The Distribution of Aromatic Products.....	52

4.3.4 Influence of Co-feeding Alcohols on Glycerol Catalytic Conversion Mechanism over Alumina.....	54
4.4 Co-Catalytic Conversion of Glycerol and Long-Chain Paraffin over Alumina	55
4.4.1 Mass Analysis	56
4.3.2 Product Distribution.....	58
4.3.3 The Distribution of Aromatic Products.....	59
4.3.4 Influence of Co-feeding Long-Chain Paraffin on Glycerol Catalytic Conversion Mechanism over Alumina	60
4.4 Conclusion	63
Chapter 5- Co-Conversion of Glycerol and n-C ₁₆ to Gasoline-Range Aromatics over Alumina.....	67
5.1 Scope of Work	67
5.2 Individual Catalytic Cracking of Normal Hexadecane	67
5.3 Co-Processing Glycerol and Normal Hexadecane with Different Composition Ratios	69
5.3.1 Effect of Co-Feeding on Conversion	70
5.3.2 Aromatization of glycerol in the presence of hexadecane	71
5.3.3 Oxygen Distribution among Formed Products	76
5.3.4 Influence of n-C ₁₆ on Glycerol Catalytic Conversion Mechanism over Alumina	77
5.3.5 Effect of Glycerol-Hexadecane Ratio on Aromatic Compounds Distribution	80
5.4 Effect of Temperature on Co-Catalytic Conversion of Glycerol and Hexadecane	83
5.5 Conclusion	87
Chapter 6- Conclusion	89
6.1 Conclusion	89
6.2 Recommendation for Future Work	91
References.....	93

Vita

List of Tables

Table 1- 1 Canada’s GHG emissions by economic sector (Mt CO ₂)	2
Table 1- 2 Canada’s ethanol and biodiesel annual production	5
Table 2- 1 Comparison between catalytic conversions of lignin over alumina and ZSM-5	17
Table 3- 1 Physical properties of pure glycerol	36
Table 3- 2 Catalyst characterization and properties.....	38
Table 4- 1 mass distribution in the individual catalytic conversion of glycerol at 470°C	46
Table 4- 2 Mass distribution of products in the glycerol-alcohol runs	51
Table 4- 3 Distribution of selectivity to desired and undesired products in the glycerol- alcohol runs.....	52
Table 4- 4 Mass distribution of products in the glycerol-long chain paraffin runs	57
Table 4- 5 Distribution of selectivity to desired and undesired products in the glycerol-long chain paraffin runs	58
Table 4- 6 Selectivity to desired and undesired products before and after co-feeding	65
Table 5- 1 Oxygen distribution among different phases through hexadecane and glycerol co-feeding runs.....	77

List of Figures

Figure 1- 1 Global average temperature (a) and global percentage of CO ₂ [3]	1
Figure 1- 2 the Fluctuation of crude oil price since 2006	4
Figure 1- 3 Comparison of petroleum-based fuel, first, and second generation biofuel.....	6
Figure 1- 4 Transesterification process of triglyceride to form biodiesel (fatty ester)	7
Figure 1- 5 Simplified Process Flow Diagram of transesterification process	8
Figure 1- 6 Industrial application of purified Glycerol [23].....	10
Figure 2- 1 Simplified reaction pathway for converting glycerol to aromatics over HZSM-5 [43].....	23
Figure 2- 2 Mechanism of glycerol dehydration on Lewis acid sites	26
Figure 2- 3 Production of aromatics and paraffins as a function of Zn loading by IE method, operational condition: 400°C, 300 psig, and W/F 3h [43].....	30
Figure 3- 1 Fixed-bed reactor for glycerol catalytic conversion evaluation	40
Figure 4- 1 organic product fraction in the liquid phase of the 100% glycerol run.....	46
Figure 4- 2 product distribution of glycerol catalytic conversion over alumina at 470°C	47
Figure 4- 3 Aromatic products distribution of glycerol catalytic conversion over alumina at 470°C	48
Figure 4- 4 proposed reaction pathway for the individual catalytic conversion of glycerol over alumina at 470°C	49
Figure 4- 5 Organic product fraction in the liquid phase of glycerol-alcohol runs	51
Figure 4- 6 Aromatic products distribution after introducing 25% (a) methanol and (b) ethanol next to glycerol over alumina at 470°C.....	53
Figure 4- 7 Organic product fraction in the liquid phase of glycerol-long chain paraffin runs	57
Figure 4- 8 Aromatic products distribution after introducing 25% (a) dodecane and (b) n-C16 next to glycerol over alumina at 470°C.....	60

Figure 4- 9 Simplified influence of co-processing long-chain paraffin on the reaction...	63
Figure 4- 10 Comparison of liquid phase distribution before and after co-feeding.....	65
Figure 4- 11 Aromatic compounds distribution before and after co-feeding	65
Figure 5- 1 Catalytic cracking of hexadecane over alumina at 470°C, phase yield (a), major products selectivity (b), and carbon fraction of organic phase (c).....	69
Figure 5- 2 Influence of co-feeding glycerol and hexadecane on conversion	71
Figure 5- 3 Influence of co-feeding hexadecane and glycerol on product distribution, phase yield (a), products selectivity (b), and gaseous products selectivity (c).	74
Figure 5- 4 Influence of co-feeding hexadecane on product distribution, phase Y_i (a), products S_{i1} (b), and gaseous products S_i (c)	75
Figure 5- 5 proposed reaction pathway for glycerol catalytic conversion over alumina at 470°C, after introducing hexadecane.....	80
Figure 5- 6 Carbon molar fraction of aromatics for different hexadecane/glycerol ratios	81
Figure 5- 7 Influence of temperature on catalytic cracking conversion of hexadecane and glycerol over alumina	83
Figure 5- 8 Effect of temperature on (a) phase yield, (b) selectivity, and (c) aromatics distribution while co-catalytic cracking of 50/50 wt.% hexadecane and glycerol over alumina.....	86
Figure 6- 1 Simplified recommended process for co-processing free fatty acids and crude glycerol in a transesterification process	91

List of Abbreviations

PBD	Process Flow Diagram
H/C _{eff}	Hydrogen to Carbon Effective Ratio
HDO	Hydrodeoxygenation
MD	Microdowner
TPD	Temperature Programmed Desorption
LAL	Lewis Acid Site
BAL	Bronsted Acid Site
IE	Ion-Exchange Method
MTG	Methanol-to-gasoline
MGTG	Methanol-and-glycerol-to gasoline
GC/FID	Gas chromatography with flame ionization detector
GC/MS	Gas chromatography and mass spectrometry
RGA	Residue Gas Analyzer
TMB	Trimethylbenzene
n-C ₁₆	Normal Hexadecane

Nomenclature

W/F	Space time
Y_i	Yield
S_i	Selectivity
F_i	Aromatics Carbon Fraction
\bar{Y}_i	Yield per 1 Unit of Glycerol
\bar{S}_i	Selectivity per 1 Unit of Glycerol
$\overline{H/C}_{\text{eff}}$	Integrated H/C effective Ratio

Chapter 1- Introduction

1.1 Disadvantages of Dependence on Fossil Fuels

Nowadays, it is accepted worldwide that excessive relying on fossil fuel-based supplies for many of industrial demands is not a rational decision. There have been a wide variety of principles and bases published so far to support this claim [1]. However, here a few of more tangible reasons are noted:

A) Rising environmental concerns (short to long term effect), pollution is probably the most noticeable disadvantage of fossil fuels. Burning fossil fuels can negatively affect the global warming, which is significantly harming the ecosystem. It is a proven fact that gases released from burning fossil fuels, especially carbon dioxide, is one of the major responsible factors for global warming. Increase in temperature of earth has already led to melting of polar ice lands and rise in the sea levels. Continuing in this condition might result in some serious consequences in the near future [2]. Fig. 1-1 represents the average trend of global warming effect.

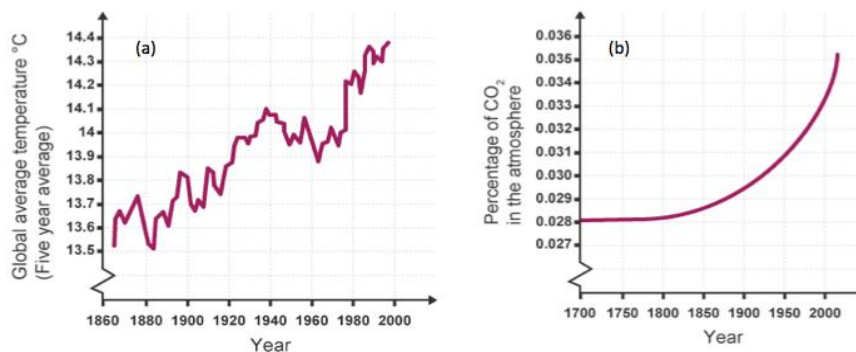


Figure 1- 1 Global average temperature (a) and global percentage of CO₂ [3]

Table 1-1 indicates the Greenhouse Gas (GHG) emissions in Canada from 1990 to 2011, derived from Environment Canada [4]. Emissions through Transportation and Oil and Gas sectors are the largest contributors in Canada's GHG emissions, representing 44% of overall GHGs. Hence, it seems necessary to make more effort on seeking alternatives in burning fuels for these two classes.

Table 1- 1 Canada's GHG emissions by economic sector (Mt CO₂)

Mt CO₂ Equivalent	1990	2000	2005	2011
Transportation	128	155	168	170
Oil and Gas	121	150	162	163
Electricity	94	129	121	90
Buildings	70	82	84	84
Trade Exposed Industries	93	85	87	78
Agriculture	54	66	68	68
Waste and Others	50	51	49	49
National GHG Total	591	718	737	702

B) Insecurity of energy source (long term), although no research can exactly predict when supplies of fossil fuels will be exhausted, the dilemma of when the resources of non-renewable energy supplies will be over is still a credible problem worldwide. Crude oil, coal, and gas are the main resources of energy supply in the world [5]. The World Energy Outlook (WEO) claimed in 2008 that energy generated from these resources would remain as the major source for a long time and is still expected to meet about 84% of energy demands in 2030 [6].

On the contrary to the claim of WEO, Shafiee et al in 2009 mathematically

computed the fossil fuel reserves depletion time and reported that oil, coal, and gas will diminish in 35, 107, and 37 years respectively [7]. Different predictions and research results might be due to the variation of price and demand of fossil fuels throughout the months and years. Regardless, it is commonly believed that renewable and environmental-accepted alternatives are needed to substitute with the non-renewable energy resources.

C) Economical fluctuations of oil and gas price (short term), oil and gas are two leading contributors in Canadian economic growth. Although rising in the crude oil price is usually considered as the main factor to pay more attention to other alternative fuels, negative growth in the economy due to a significant drop in the price could also be a key point to focus more on substitutions for non-renewable resources.

Too much dependence of Canadian economy on oil and gas industry can easily influence on other related industries such as food and petrochemical factories negatively. According to Canadian Statistics, over 1,000,000 individuals lost their jobs in 2015 mostly because of oil and gas industry crisis [8]. Fig. 1-2 indicates a trend of crude oil price in the past 10 years derived from Organization of Petroleum Exporting Countries (OPEC) [9]. The price has been swinging from the lowest value of 26\$/Barrel to the highest value of 147\$/Barrel. Seeking alternative resources to substitute the industrial feedstock and fuels might contribute to mitigate the high dependency of the economy on oil and gas industry.

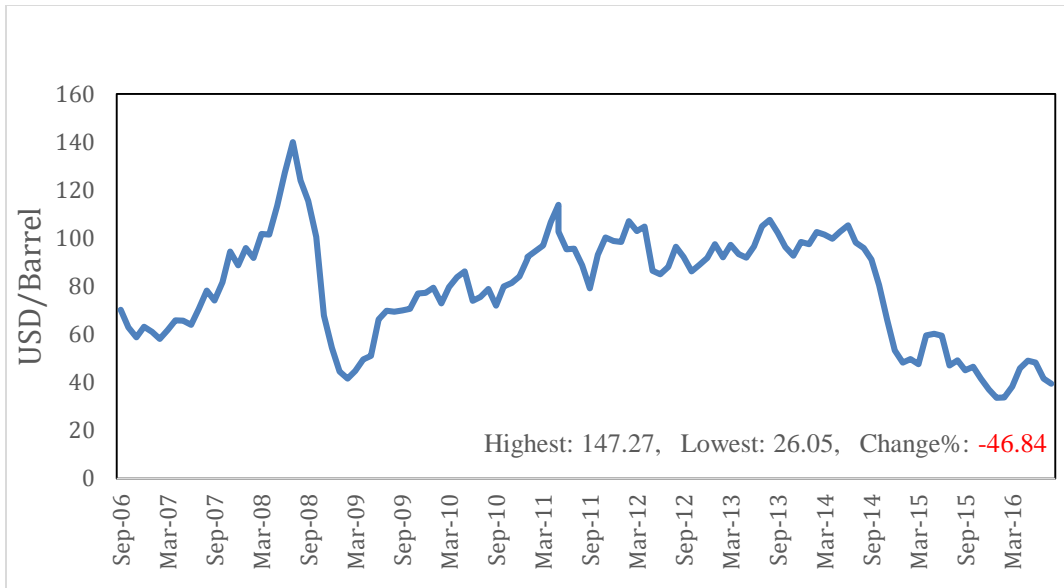


Figure 1- 2 the Fluctuation of crude oil price since 2006

1.2 Biofuel, Alternative Source of Energy

Canadian government has introduced its goal to reduce the emissions of greenhouse gases by 30% till year 2030 [10]. As it was discussed earlier, transportation sector has the highest GHGs emission in Canada. Hence, a significant progress has been made in founding domestic renewable fuels industries. Biofuels- whether biodiesel or ethanol- can play a significant role in achieving the GHGs emission reduction target. In 2007, Canadian Federal Government presented its renewable fuel usage strategy, which announced the mandated requirement for use of ethanol and biodiesel [10]. Canada's renewable fuel standard obligates a blend of 5 percent ethanol into the gasoline pool and a blend of 2 percent biodiesel in the distillate pool (diesel) [11].

Canada's renewable fuels industry has substantially grown because of the mentioned legislation. By the end of 2014, Canada was domestically producing almost 1.3 billion liters of ethanol and around 400 million liters of biodiesel annually. Table 1-2

clearly shows the growth of renewable fuels production since 2010 derived from Canada Biofuel 2015 annual report [12]. Ethanol has considerably higher production comparing to biodiesel as it also has a wide variety of applications in other industries as well.

Table 1- 2 Canada’s ethanol and biodiesel annual production

Calendar Year (Beginning)	2010	2011	2012	2013	2014	2015
Ethanol Production (million liters)	1,530	1,790	1,780	1,815	1,820	1,820
Biodiesel Production (million liters)	115	120	100	140	300	395

Moreover, a separate analysis indicates that biofuels generate significantly lower greenhouse gas (GHG) emissions such as the emission of carbon dioxide, comparing to the traditional fossil fuels. In comparison with the normal gasoline, life-cycle GHG emissions for conventional grain ethanol are 62 percent lower. For biodiesel, this rate is even higher, and it potentially would lead to up to 99 percent GHG reductions [13].

1.3 Biofuel Production Processes

As it was described earlier, ethanol and biodiesel are considered as the main biofuels in Canada to mitigate the current fossil fuels issue. So-called first generation, second-generation biofuels, and fossil fuels are summarized and compared in Fig. 1-3 [14]. Moreover, the production process of biodiesel as the main first generation biofuel is briefly explained and detailed why it is important to further process the crude glycerol.

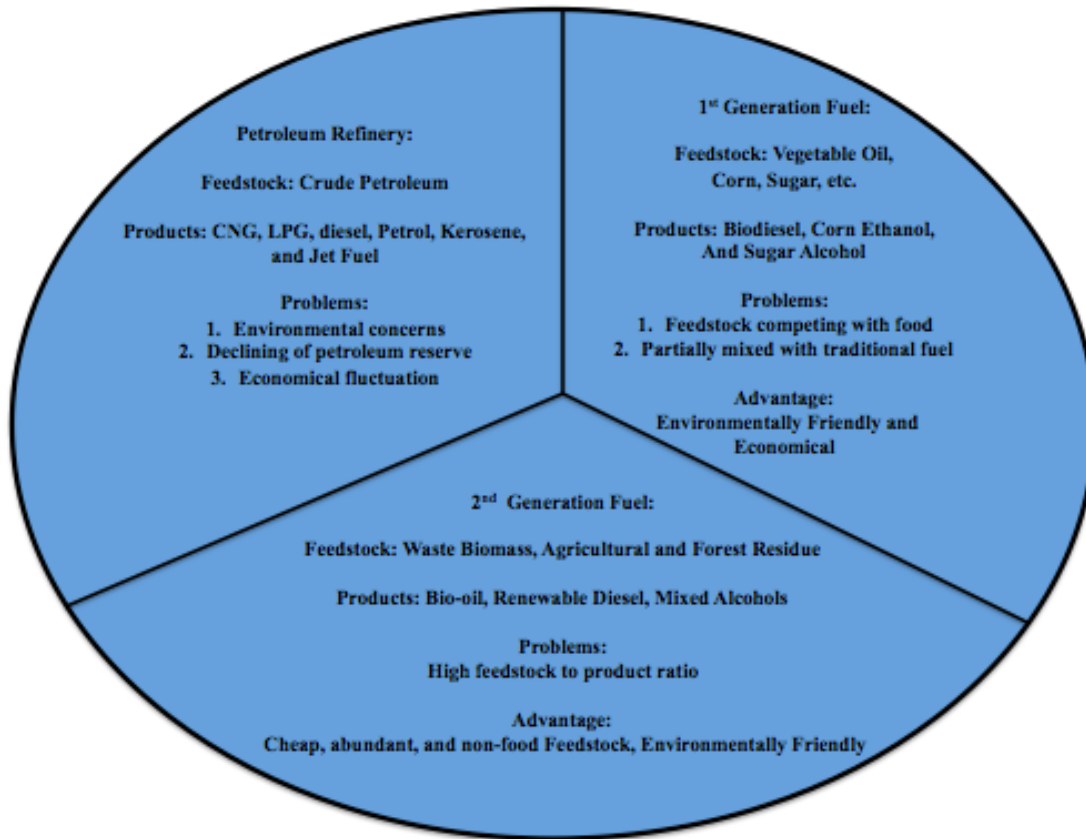


Figure 1- 3 Comparison of petroleum-based fuel, first, and second generation biofuel

1.3.1 Biodiesel Production Process

Biofuel generation processes are generally classified based on their initial feedstocks and final products. Biodiesel (bio-esters), ethanol, and biogas are the three main types of first generation biofuels, which are produced in large quantities world wide [14]. The first generation liquid biofuels are generally processed from sugars, seeds, or vegetable oils [15]. Before further describing the common processes for producing first generation biofuels, it is notable that the main drawback for the production of this type of biofuel is the feedstock. It is debated that the use of sugars or corns as feed in the process is questionable as they conflict with the food supply [16]. This challenge will likely increase the production cost since it should compete with the food industry. Such obstacles favored

the search for non-edible (non-food) biomass as feedstocks for the production of biofuels, which led to the second generation biofuels.

Various technologies are already being used in order to produce first generation biofuels from renewable sources. The conversions of sugar containing crops and cellulosic biomass to ethanol through fermentation process, and anaerobic digestion of biomass in the absence of oxygen to form biogas are some of the common processes [14] However, the most well-known technology among the first generation biofuels would be the transesterification process (Fig. 1-4).

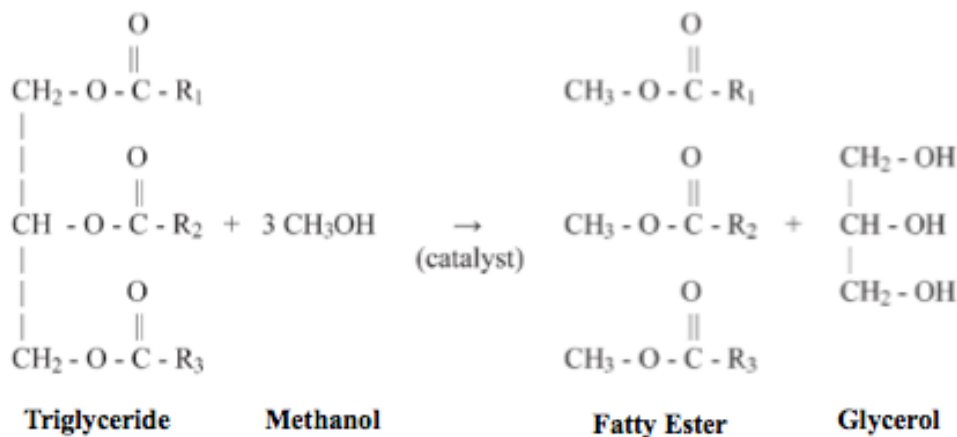


Figure 1- 4 Transesterification process of triglyceride to form biodiesel (fatty ester)

Fatty Ester is commercially known as biodiesel, which is produced through the chemical reaction between triglyceride (provided by animal fat or vegetable oil) and an alcohol [17]. The product is a two-phase stream that includes an organic phase (biodiesel-rich) and an aqueous phase (glycerol-rich). In case of using methanol as the alcohol in the process, the fatty ester is named methyl ester. The use of heterogenous catalyst is common in the transesterification process. Solid acid catalyst can enhance in both transesterification

of triglycerides and esterification of free fatty acid to form fatty esters [18].

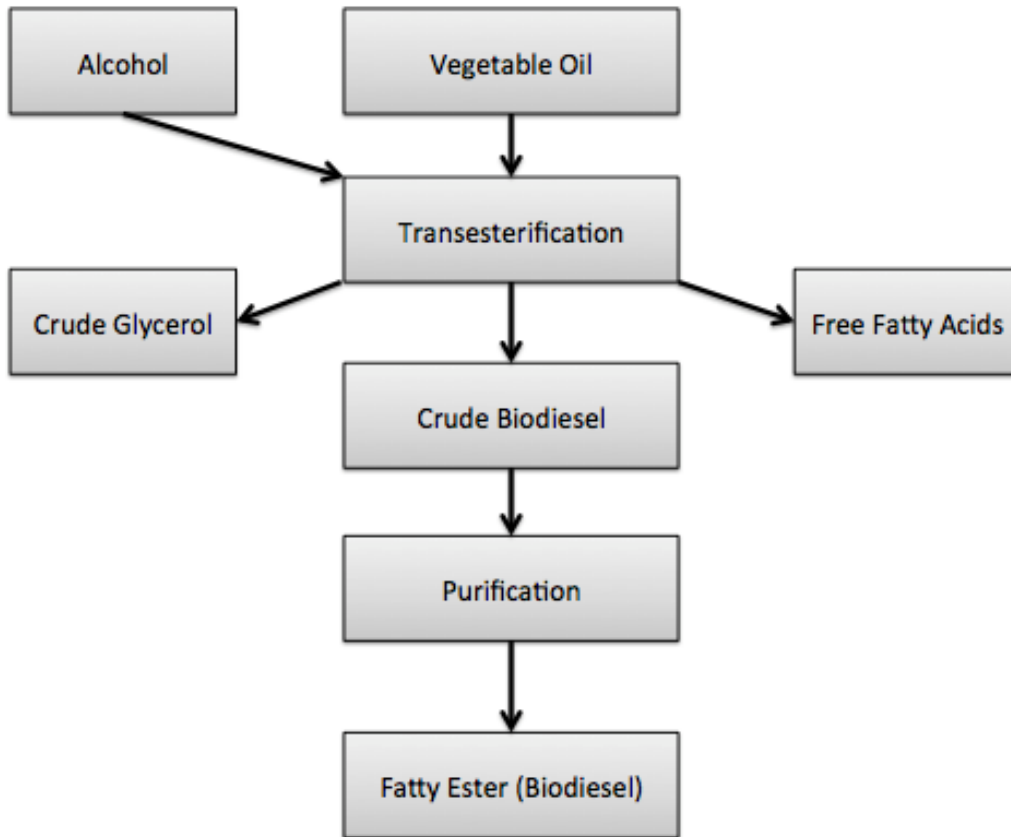


Figure 1- 5 Simplified Process Block Diagram of transesterification process

A simplified Process Block Diagram (PBD) of the transesterification process is presented in Fig. 1-5. As it is shown in the diagram, crude glycerol is also formed next to glycerol in the commercial process. The general benefits of biodiesel and its advantages over petro-diesel have been studied by different researches so far [15, 19, 20]. Crude glycerol as the main by-product of the process is gaining more attention these days to evaluate, if there is any potential future for it as an industrial feedstock or it is mostly faced as a drawback for the production of biodiesel.

1.3.2 Glycerol

Glycerol is almost entirely produced from the reactions of triglycerides, and only about 12% of the global production of glycerol is formed synthetically. The yearly worldwide production of glycerol is estimated to be approximately 750,000 tons [21].

The growth of biodiesel plants can greatly depend on the utilizing of the formed crude glycerol as the main by-product. In a biodiesel production plant, crude glycerol is approximately 10 wt.% of the generated biodiesel. Hence, assuming the yearly production of 10 M metric tons, 1 M metric tons of glycerol is by-produced and becoming a bulk renewable feedstock.

The saturation of glycerol in the market can lead to a continuous decrease of glycerol price, which would potentially result in the increase of biodiesel end cost [22]. On the other hand, disposing the crude glycerol can definitely rise environmental concerns that might lead to the restriction of biodiesel production growth as well.

Glycerol is a valuable by-product can be greatly utilized as a renewable resource of energy and material. It has a wide range of industrial applications as shown in Fig. 1-6. It is commonly useful in different areas such as pharmaceutical, personal care, and food.

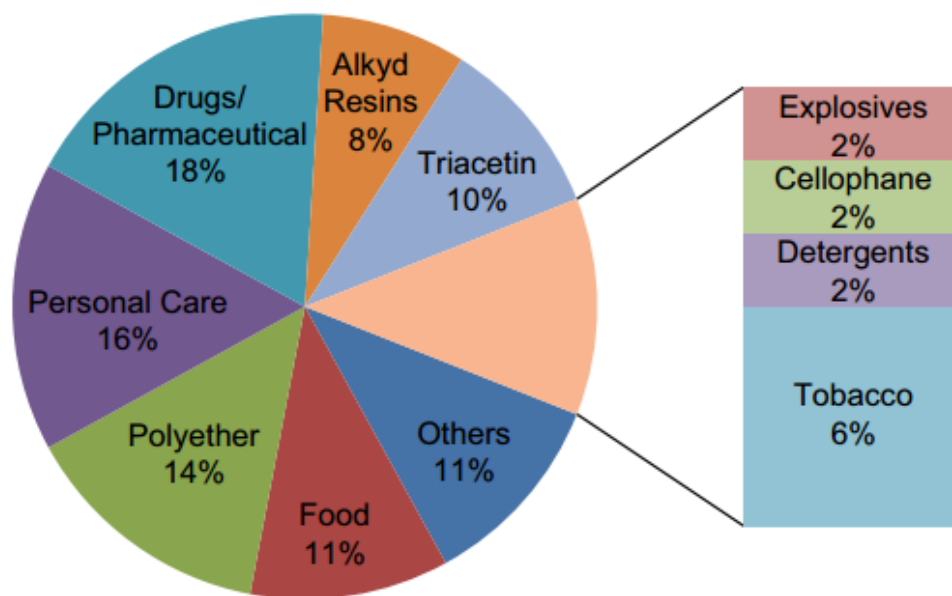


Figure 1- 6 Industrial application of purified Glycerol [23]

The major drawback of applying the crude glycerol derived from biodiesel production plants, as feedstock for the above-mentioned industries is the quality. It is reported that the glycerol quality of the crude glycerol from biodiesel production process is between 60 wt.% and 70 wt.%, whereas the quality reaches high up to 90 wt.% in reactions like saponification and hydrolysis[24].

To mitigate the issue, different purification methods such as distillation, filtration, and chemical treatment have been taken [21]. In order to achieve high efficiency in the preparation of the crude glycerol to use as feedstock for more sensitive industries such as drugs and personal care, often two or more methods are combined. Combing the alcohol recovery step by distillation and salt removal stage by adsorption using activated carbon is a common purification process [21, 25]. The purification step of the formed glycerol through biodiesel to convert to usable state is often difficult and costly.

However, glycerol is a very active molecule and would convert to value-added

product under feasible reaction conditions. The formed products via glycerol chemical reactions could be considered as potential feedstocks for different petro-chemical industries. For example, catalytic oxidation of glycerol results in formation of a wide variety of compounds such as dihydroxyacetone and glyceraldehyde [25]. Glycerol can also be converted to 1,3-propanediol through reactions such as hydrogenolysis and dihydroxylation [26]. Crude glycerol would be considered as an interesting feedstock for this purpose as the production of 1,3-propanediol is limited and costs are high [21]. Propenal is another advantageous compound can be formed via 1-step dehydration of glycerol over solid acid [27].

1.4 Research Objectives

To contribute in the growth of biofuels production, especially biodiesel formation processes, it seems crucial to utilize the applications of the by-products to reduce the capital investments. It was elaborated earlier that highly efficient purification of crude glycerol as the main by-product of biodiesel production process is relatively costly and difficult. On the other hand, converting crude glycerol to value-added products and applying them in other industries can be an effective solution.

In this work, the potential ways of utilizing glycerol in generating liquid aromatic compounds, focusing on gasoline-range aromatics such as toluene, xylenes, and trimethylbenzenes is studied.

In the chapter 2, some similar work on converting glycerol to value-added chemicals is reviewed. Moreover, it is trended that why oxygenated compounds including glycerol have a high tendency to undergo cyclization and aromatization reactions. Different

proposals on enhancing the final products' aromaticity such as catalyst modification and the glycerol media dilution method during the glycerol conversion processes are critically reviewed. It is also briefly evaluated why it is beneficial to focus on producing light aromatic compounds from crude glycerol.

Only a few studies on the catalytic conversion of glycerol over Lewis acid catalysts have been performed so far, and most of the studies are dominated by the use of zeolite-based catalysts that are rich in Bronsted acid site. Hence, in the chapter 4, a detailed study on the catalytic conversion of glycerol over alumina (Lewis-acid) catalyst is presented. Consequently, to enhance the formation of liquid organics, especially gasoline-range aromatics, and suppress the drawbacks of individual catalytic conversion of glycerol, co-processing method is evaluated. Unlike the similar researches completed by peers, it is focused on keeping the glycerol as the major feed and the second compound is introduced as a minor feed, which constitutes only 25 wt.% of the total feedstock. Methanol and ethanol as compound models for alcohols, and dodecane and normal hexadecane as compound model for long-chain paraffin are fed to the process next to glycerol separately. Then, results are rigorously compared with each other and the individual catalytic conversion of glycerol. So, it is discussed how potentially the introduced co-feeds would lead to achieve the main target, which is increasing the aromaticity in the final product and decrease the formation of undesired carbon deposit on the catalyst surface.

In the chapter 5, the influence of co-processing normal hexadecane next to glycerol over alumina is evaluated in more details. As it was concluded in the chapter 4 that co-feeding n-C₁₆ has the highest efficiency among the co-fed compounds, an effort is made to propose that how hexadecane would likely affect the reaction pathway of glycerol over

alumina. Later on, the influence of the operational temperature on the performance of co-processing glycerol and hexadecane is also studied to find an optimum point, which results in the higher formation of light aromatic compounds.

Finally, chapter 6 summarizes the main conclusions of this work and gives recommendations on how to implement this technology industrially.

Chapter 2- Literature Review

As was mentioned earlier in chapter 1, glycerol is the main by-product of biodiesel production process through transesterification method. In this chapter, the dependency of catalytic conversion on the type of the oxygenated compounds is evaluated at first. Later on the current approaches of the catalytic conversion of glycerol to valuable products including gasoline-range aromatics over Bronsted acid and Lewis acid catalysts are studied and compared. Innovative methods of converting glycerol to valuable aromatics are also reviewed. Finally, it is described why it is beneficial to form light aromatics from glycerol.

2.1 Catalytic Conversion of Oxygenated Compounds to Olefins and Aromatics

Catalytic conversion of biomass derived oxygenated compounds is one of the beneficial processes to synthesize valuable chemicals that are currently obtained from fossil fuels. The activity of oxygenated hydrocarbons derived from biomass pyrolysis over solid acid catalysts is relatively high; however, the promotion of the reaction selectivity towards less oxygenated compounds is a great challenge [28]. The formation of coke on the catalyst surface, as the most undesired reaction, occurs while processing the oxygenated hydrocarbons, which competes with the conversion of the feedstock to value-added products like liquid aromatics and olefins.

Precursors of coke carbonized on the catalyst are mostly polyaromatic compounds with the boiling point in the range of 450-650 °C that will cause the catalyst deactivation through blocking the acid sites and pores [29]. On the other hand, aromatic hydrocarbons are highly desirable products since they can be used as feedstock for the production of

several valuable chemicals and polymers.

Catalytic conversion of biomass derived oxygenated hydrocarbons greatly depends on the type of the feedstock, catalyst properties such as acidity and porosity, and operational conditions [28].

2.1.1 Impact of Oxygenated Compound Structure on Selectivity to Olefins and Aromatics

The properties of oxygenated hydrocarbons, whether physical or chemical, can directly affect the reaction selectivity toward products such as olefins and aromatics. Hydrogen to carbon effective (H/C_{eff}) is an important factor that influences the reaction behavior. H/C_{eff} is defined by the following equation [30]:

$$H/C_{\text{eff}} = \frac{H - 2O - 3N - 2S}{C}$$

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

Petroleum derived hydrocarbons usually have higher H/C_{eff} ratio than oxygenated compounds derived from biomass. This ratio is ~ 2 for highly paraffinic hydrocarbons and slightly > 1 for aromatic compounds. But, the H/C_{eff} ratio for carbohydrates, sorbitol, and glycerol (oxygenated compounds) are 0, 0.33, and 0.67 respectively [31]. It is reported that generally catalytic conversion of feedstocks with H/C_{eff} ratio below 1 (mostly oxygenated compounds due to high content of oxygen) has high tendency to form carbonized compounds on the catalyst surface [30]. Low H/C_{eff} ratio of feedstock would likely decrease the amount of hydrogen that can be produced from coke, which will directly affect

the production of liquid organic phase. For instance, the coke formation of carbohydrates will not generate any hydrogen [31].

Generally, reactions such as hydrogenation, hydrogen transfer, decarbonylation, and decarboxylation can increase the H/C_{eff} of the products and lead to enrich the liquid organic phase compounds like aromatics [31]. However, dehydration mechanism does not necessarily increase the overall H/C_{eff} of the products. In case the dehydration reaction is facilitated by internal intermediates (not from external donors), effective hydrogen to carbon ratio does not change in the dehydrated product. Hence, the removal of oxygen through reactions like decarboxylation and decarbonylation is preferred over dehydration as the deoxygenation occurs without hydrogen removal.

2.1.2 Impact of Catalyst Characteristics on Selectivity to Olefins and Aromatics

In order to utilize the catalytic conversion of biomass-derived oxygenated hydrocarbons towards the maximum aromatics selectivity and minimum carbon deposit formation, catalyst acidity caused by Bronsted and Lewis acid sites as well as shape selectivity are the two leading factors, which need to be optimized [28].

Zeolite-based catalysts are the most common solid acids used for cracking reactions due to their appropriate content of Bronsted and Lewis acid sites. Among them, HZSM-5 zeolite is considered as an effective catalyst for the conversion of oxygenated compounds to aromatics [32]. HZSM-5 catalyst includes strong acid sites (Bronsted acid sites), and decreasing its Si/Al ratio (increasing the number of acid sites) would likely enhance the formation of liquid aromatics.

Table 2- 1 Comparison between catalytic conversions of lignin over alumina and ZSM-5

Feedstock	Catalyst	Water ^b	Oil ^b	Gas ^b	Solid ^b	Aromatics ^b
Lignin	Alumina (S_{BET} : 215 m ² /g)	32.47	5.46	28.23	33.85	0.59
	ZSM-5 ^a (S_{BET} : 138 m ² /g)	27.70	20.82	25.86	25.70	1.186

a) Diluted with silica-alumina (includes 30 wt.% crystalline zeolite)

b) Wt.% of feed

Table 2-1 represents a comparison between the catalytic conversions of lignin over alumina and ZSM-5 [33]. Although alumina has relatively higher surface area, the selectivity of reaction towards liquid aromatics over ZSM-5 catalyst is significantly higher. Moreover, the formation of undesired streams such as water and carbon deposit is lower over the latter catalyst than alumina.

Although number of acid sites present in a porous catalyst is also an important factor to enhance the selectivity of liquid aromatics and should be modified, the need for strong acidity on the catalyst seems to be more crucial. Stephanidis et al. reported that in catalytic pyrolysis of beech wood over silicate with Si/Al ratio of > 1000 had higher selectivity toward aromatics compared to over mesoporous aluminosilicate Al-MCM-4 with the Si/Al ratio of 30. The reason for this is that even though the selected silicate has very few of acid sites, it contains strong Bronsted acid sites. But Al-MCM-4 has weak acid sites, despite having large number of acid sites [34].

Catalyst pore-opening size is also another determining factor in order to enhance the liquid aromatic production. Pore size has an impact on the mass transfer of large molecules over the catalyst and can restrict them from the diffusion into the pores and interacting with acid sites [28]. However, it seems the selection of a suitable pore-size

opening depends on the type of the feedstock. For example, in the catalytic fast pyrolysis of lignin, selecting a catalyst with larger pore size leads to higher liquid organic stream and less coke formation. But, in an experiment facilitated by Corma to evaluate the catalytic cracking of glycerol in a fixed-bed reactor over six different catalysts, it was found that ZSM-5 led to the lowest coke yield and the significantly higher aromatic yield. This result was attributed to the prevention of smaller pore size of the catalyst from the formation of polyaromatic compounds that act as carbon deposit on the catalyst [31].

2.1.3 Impact of Reaction Condition on Selectivity to Olefins and Aromatics

Enhancing the production of valuable products such as olefin and liquid aromatics can be facilitated by the optimization of operational parameters. Increasing the selectivity to olefins and aromatics can be achieved either directly or by decreasing the formation of undesired streams like coke. For instance, it is reported that lowering the residence time would likely decrease the coke yield due to the reduction of excessive condensation and polymerization reactions [35]. However, there is no direct relation between operational temperature and coke formation as increasing the temperature could decrease the catalytic coking but would likely increase the thermal coking rate.

Adjusting reaction conditions including temperature, catalyst to feed ratio, and heating rate can directly optimize the selectivity toward liquid aromatics [28]. High catalyst to feed ratio and heating rate can significantly improve the production aromatics. For example, it was experimented that increasing the HZSM-5 (catalyst) to glucose (feed) ratio from 1.5 to 19 enhanced the formation of aromatics by 18% [36]. Raising the operational temperature in the latter work from 400°C to 600°C increased the carbon yield of aromatics from 10% to 30%. However, in the selection of suitable temperature, it should be noted

that aromatization reactions are exothermic and could be restricted at higher temperatures. It was reported by Corma that during the catalytic conversion of glycerol over ZSM-5 at 500°C, the aromatics yield had increase with conversion, but decreased at 600°C and 700°C [31].

Providing external proton-donors and reactive components to the process of catalytic conversion of oxygenated hydrocarbon is also another contributing method that adjusting it would enhance the production of liquid aromatics. Catalytic hydrotreating under high-pressure hydrogen (mostly in the scale of 30-140 bar) or diluting the feedstock with hydrogen donor solvents are two common methods currently being used for upgrading the biomass-derived oxygenated compounds [28]. Operating the reaction at atmospheric pressure with the use of hydrogen donor solvents will increase the H/C_{eff} ratio in the process. This method seems to be more economical and safer method compared to hydrodeoxygenation (HDO). Methanol is a suitable solvent to supply hydrogen and proton-donor intermediates in the catalyst, which would lead to decrease of the coke formation and increase the liquid organic phase production. Zhang et al. reported that the addition of methanol next to pinewood with the integrated H/C_{eff} ratio of 1.25 during the catalytic fast pyrolysis at 450°C enhanced the carbon yield of gasoline-range aromatics by 15% [37].

Co-feeding olefins with biomass-derived oxygenates can also affect the production of liquid aromatics in the process. Carlson et al. performed a study to evaluate the influence of the addition of olefins such as ethylene and propylene on the catalytic conversion of furan [36]. It was observed that co-feeding propylene/furan with the ratio of 0.3 did not significantly change the carbon yield of aromatics, but remarkably affected the distribution of aromatics. Co-processing propylene with furan substantially increased the selectivity of

light aromatics like xylene and toluene and suppressed the formation of indene, benzofuran, and naphthalene.

2.2 Catalytic Conversion of Glycerol to Olefins and Aromatics

Several researches have been investigated the different ways of catalytic conversion of glycerol to value-added chemicals such as propenal, acetol, and alkyl aromatics. Majority of the studies belong to the catalytic conversion of glycerol over zeolite-based catalyst (rich in Bronsted acid site), and only few analysis have been made to evaluate the performance of Lewis acid catalysts through the glycerol catalytic conversion.

2.2.1 Catalytic Conversion of Glycerol over Bronsted Acid-Rich Zeolites

Glycerol can be converted into propenal, acetaldehyde, and olefins over zeolites. Corma et al. performed a study on the catalytic conversion of glycerol/water mixture over zeolite-based catalysts in continuous and fixed-bed reactors [38]. Continuous fluidized-bed reactor led to higher efficiency as it allowed better mass and heat transfer. Different operational parameters and catalysts were applied to optimize the formation of propenal from glycerol.

Table 2-2 represents the influence of temperature on the production of oxygenates and hydrocarbons through the glycerol catalytic conversion of glycerol over ZSM-5 at a microdowner (MD) reactor [38]. The highest yield of propenal was achieved at 350°C with the carbon molar selectivity of 58.8%. Increasing the temperature to the range of 500°C to 700°C remarkably decreased the formation of propenal and other oxygenated liquid. However, selectivity to carbon dioxide and organic gases (alkanes and olefins) rose

significantly. This finding indicated that high-temperature operation is suitable for light-olefin production, but not for the formation of oxygenates.

Table 2- 2 Effect of temperature on glycerol conversion in Microdowner (MD) reactor (50 wt.% glycerol aqueous solutions)

Temperature (°C)	350	500	650	700
Catalyst	ZSM-5	ZSM-5	ZSM-5	ZSM-5
Molar Carbon Selectivity (%)				
CO ₂	2.6	9.7	18.0	42.0
CO	0.8	6.3	8.8	5.1
C ₁ -C ₄ alkanes	<0.1	0.5	3.3	12.9
C ₂ -C ₄ olefins	1.8	10.7	20.4	30.5
Propenal	58.8	23.2	11.0	0.4
Acetaldehyde	8.5	15.2	20.7	1.0
Others CHO	14.7	10.0	4.43	0.4
Coke	12.2	17.7	5.7	3.2

Hoang et al. studied the influence of the pore geometry of different zeolite-based catalysts on the conversion of glycerol to gasoline-range alkyl-aromatics at 300-400°C [39]. Even though throughout all the studies, propenal was the major glycerol dehydration product at low space time (W/F), the pore structure significantly influenced the final products distribution. For example, it was found that one-dimensional HZSM-22 with the ring opening of 10-MR is suitable for the production of propenal with the maximum yield of 86% at 400°C and 0.5hrs W/F, but no aromatic formation. On the other hand, 60% carbon yield of aromatics was obtained over the three-dimensional HZSM-5

catalyst with the ring opening of 10-MR under the same operational temperature and 4hrs W/F, but the propenal production yield diminished to 10%.

These findings indicated that the configuration of the catalyst internal pores would play a significant role in the formation of aromatics from glycerol. The pore intersection sites present at three-dimensional HZSM-5 would facilitate the aromatization reactions as they have a space larger than pore channels, providing enough room for the reaction [39].

A detailed study was conducted by Tamiyakul to evaluate the impact of HZSM-5 acidity on the production of aromatics from glycerol. Moreover, the potential reaction pathway for the catalytic conversion of glycerol to aromatics over HZSM-5 catalyst was proposed [40]. To investigate the effect of acidity, five different Si/Al ratios of 23, 30, 50, 80, and 280 were tested at 400°C and 300 psig. The tendency to the formation of aromatics decreased in the order of HZSM-5 (30) > HZSM-5 (50) > HZSM-5 (80) > HZSM-5 (23) > HZSM-5 (280). Hence, it was concluded that generally, increase in the acidity of the catalyst (lower Si/Al ratio) results in higher aromatic production. However, it was noted that even though HZSM-5 (23) contained the highest Bronsted acidity among the tested ratios, it led to a small carbon yield of aromatics. Lower surface area of HZSM-5 might be a reason for this trending, as it would result in lower active surface for the aromatization reactions.

The second cause for the low carbon yield of aromatics over HZSM-5 would be the high amount of water adsorbed by the catalyst. It was claimed that the temperature programmed desorption of water (H₂O-TPD) indicated high amount of water desorbed from HZSM-5. In an acid-dehydration reaction, the presence of water can inversely affect the acidity and stability of the solid-acid catalyst [41].

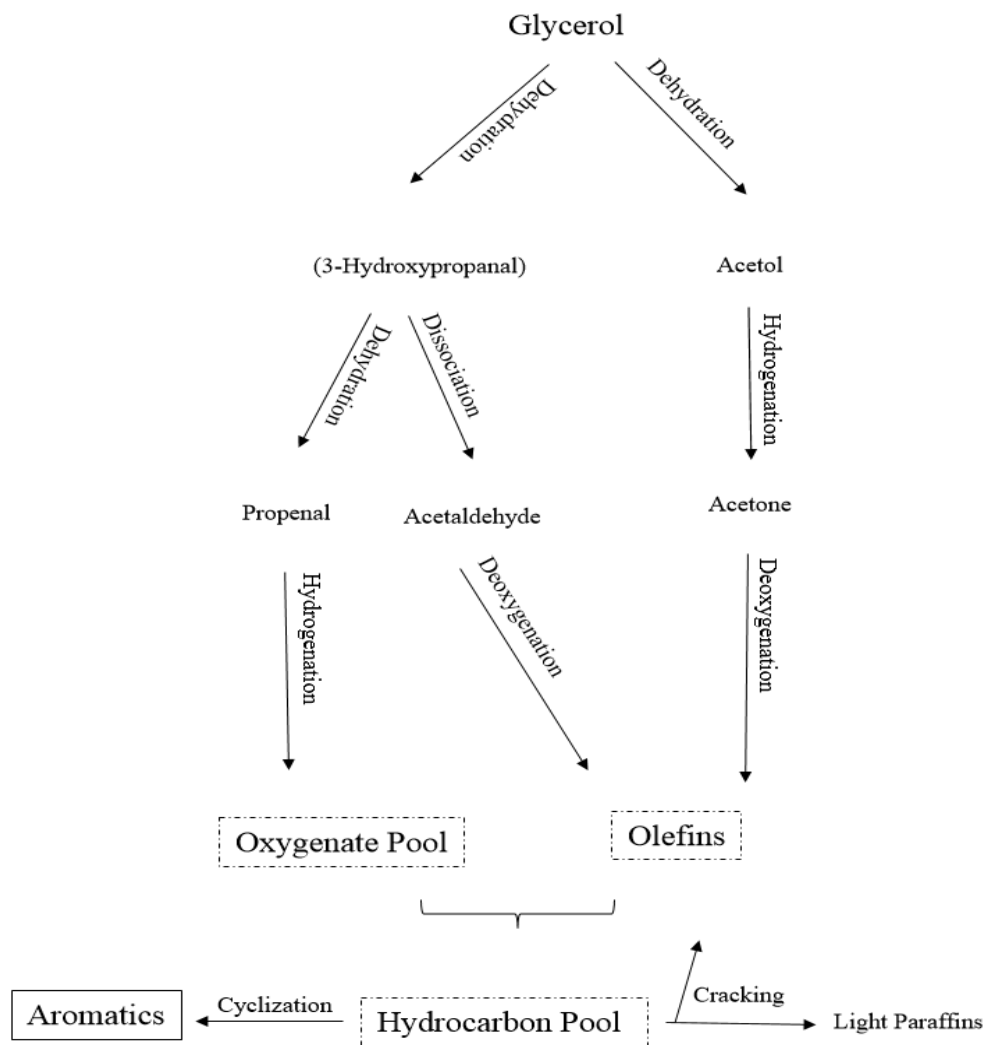


Figure 2- 1 Simplified reaction pathway for converting glycerol to aromatics over HZSM-5 [40]

The simplified reaction pathway for the catalytic conversion of glycerol to aromatics over HZSM-5 is presented in Fig. 2-1. The product mixture mainly contained propenal, acetaldehyde, and olefins in the low W/F, and included aromatics and light paraffins in the higher W/F. This distribution indicated that the first step of glycerol conversion was dehydration via the removal of central –OH and internal –OH of glycerol.

High tendency to the formation of propenal and acetaldehyde in lower contact time might be due to the high Bronsted acidity of HZSM-5 catalyst, which results in the readily removal of the central –OH group of glycerol. Lewis acid sites mainly lead to the removal of terminal –OH group and the formation of acetol [27]. In case of proper hydrogenation, acetol would later on form ketonic compounds such as acetone.

By increasing W/F, it was claimed that the hydrogenation of propenal and acetone (occurred by using coke and H-donor species over strong acidic HZSM-5 catalyst) contributed to rise in the oxygenate pool compounds and olefins and decrease in the dehydrated products including propenal. The strong tendency to form light paraffins and aromatic products at increased W/F indicated that oxygenate pool and olefins act as intermediates for the final products. These intermediates would likely react themselves or with each other via further reactions such as oligomerization, dehydration, decarbonylation, and decarboxylation and result in the formation of hydrocarbon pool in the catalyst pores. Later on, the trapped heavy hydrocarbons would reach the active sites in the zeolite and undergo mechanisms like cracking, aldol condensation, and cyclization to form light paraffins or aromatics. The catalytic conversion of glycerol over HZSM-5 (Si/Al=80) at 400°C and 300 psig resulted in around 50% carbon yield of aromatics, while the space time (W/F) reached 1hr. The produced aromatic stream mainly consisted of toluene and xylenes [40].

2.2.2 Catalytic Conversion of Glycerol over Lewis Acid Catalysts

Unlike the extensive studies have been completed so far regarding the catalytic conversion of glycerol over Bronsted acid site-rich catalysts, very few efforts have been

made on evaluating the role of Lewis acid sites. It is generally agreed that due to the nature of required acid sites, the presence of Bronsted acid site has higher importance to dehydrate glycerol to propenal, and then convert it to hydrocarbon pool and aromatics. Hence, it was mostly focused on increasing the yield of green products via tuning the Bronsted acidity over the catalyst.

Alhanash et al. tested a pure Lewis solid acid catalyst for the dehydration of glycerol [27]. The catalytic dehydration of glycerol was performed over Zn-Cr oxide catalyst at three different operation temperatures using N₂ or H₂ as inert and active carrier gas (Table 2-3).

Table 2- 3 Glycerol dehydration over Zn-Cr (1:1) mixed oxide catalyst (conversion and selectivity after 5hrs time on stream)

Catalyst	Carrier Gas	Temperature (°C)	Conversion (%)	Selectivity (%)	
				Propenal	Acetol
Zn-Cr	N ₂	275	<1		
Zn-Cr	N ₂	300	9	34	42
Zn-Cr	N ₂	350	18	30	40
0.3%Pd/Zn-Cr	H ₂	350	49	32	31

No conversion at 275°C and moderate conversion at 300-350°C would be due to the lower functionality of the Lewis acid sites at low temperatures compared to the Bronsted acid sites. However, the more important result was the remarkable carbon molar selectivity of acetol (hydroxyacetone) in moderate temperatures. On the contrary to the high tendency of glycerol catalytic conversion over zeolites to form propenal, it was observed that Zn-Cr oxide catalyst resulted in the formation of acetol as the main product. Hence, it was concluded that acetol commonly forms on Lewis acid sites, whereas propenal on Bronsted

acid sites. Use of palladium impregnated catalyst and H₂ significantly increased the glycerol conversion under the identical operational condition. The decrease in the selectivity of acetol after this change might be caused by the further hydrogenation and dehydration of acetol to form ketonic compounds such as acetone and hydrocarbons including light olefins.

During the glycerol dehydration mechanism over Bronsted acid sites, proton transfer is not limited by steric constraints, and proton acid sites can reach the internal oxygen in the glycerol that is possessing a higher negative charge and remove it as water. Furthermore, the dehydrated intermediate (3-hydroxypropanal) can lose the second oxygen through a pretty similar mechanism and result in the production of propenal. However, Alhanash stated that unlike the dehydration mechanism over Bronsted acid site, interaction of glycerol with Lewis acid sites is limited by steric constraints. Hence, Lewis acid sites would more likely reach the terminal OH groups and result in 2,3-dihydroxypropene. This intermediate would then be tautomerized to yield acetol (Fig. 2-2) [27] On the contrary to the formation of propenal over Bronsted acid sites, the second dehydration step cannot readily happen over Lewis acid sites [40]

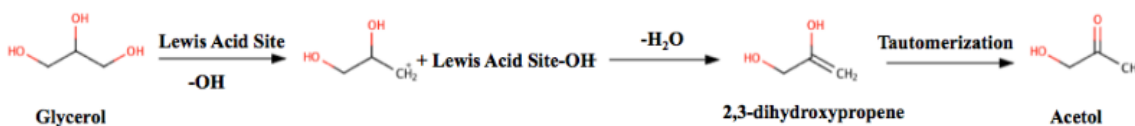


Figure 2- 2 Mechanism of glycerol dehydration on Lewis acid sites

The difficulty of further dehydration and hydrogenation over Lewis acid sites at low temperature and with use of N₂ carrier gas could attribute to the abundance of one-time dehydrated glycerol compound over Lewis acid catalyst (acetol) as the main product.

Cooperativity of Lewis Acid Sites (LAS) and Bronsted Acid Sites (BAS) on zeolites for glycerol dehydration was evaluated by Wang [42]. In this work, acetol was considered as by-product, and the role of LAS was defined to cooperate with the neighboring BAS to optimize the formation of propenal.

The strategy to alter the negative role of LAS in competing with BAS and creating acetol to the positive role of conducting in propenal production was to introduce extra-framework aluminum cations (LAS) into HZSM-5 with a high amount of BAS. This framework in the zeolite matrix would generate multifunctional active sites. Simultaneous function of the neighbored LAS and BAS would likely favor the mechanism toward the desired product.

In this work, the catalytic performance of ZSM-5 catalysts through the selective dehydration of glycerol to propenal was studied at 588 K. It was observed that the increase in the number of BAS in the prepared catalysts (from 36.7×10^{-2} mmol/g in Al/Na-ZSM-5 to 76×10^{-2} in H-ZSM-5) enhanced the carbon yield of propenal from 24.1% to 35.4%. The catalytic performance of Al/H-ZSM5 and H-ZSM5, with the same number of BAS, were also studied and compared. It was found that Al/H-ZSM5, which included multifunctional active sites, had higher tendency to produce propenal with the carbon yield of 54.4%. Hence, it was concluded that tuning the LAS and BAS together over the catalyst to work together would likely have higher efficiency in terms of propenal production than only increasing the number of BAS. It was interpreted that after initiating the dehydration reaction of glycerol over the Bronsted acid site of the zeolite catalyst by removing the internal OH group, the neighbored Lewis acid site would contribute in the removal of the second OH group and result in a higher propenal production.

2.3 Innovative Methods to Improve the Selectivity of Gasoline-Range Aromatics from Glycerol Catalytic Conversion Reactions

In order to optimize the production of liquid aromatics- especially gasoline-range ones- from the catalytic conversion of glycerol, some valuable studies have been completed so far. The promotion of the dehydrogenation metal on zeolite-base catalyst, a two-bed configuration of catalysts with two different functions of deoxygenation/hydrogenation and aromatization, and dilution of glycerol with alcohols instead of water are some of the earlier reported studies [30, 39, 40, 43].

2.3.1 The Promotion of the Dehydrogenation Metal on HZSM-5

To enhance the carbon yield of aromatics through the catalytic conversion of glycerol over HZSM-5 with the Si/Al ratio of 30 at 400°C and 300 psig, Zn was loaded on the catalyst (yZn/HZSM-5) via Ion-Exchange (IE) method[40]Zn promoter is usually applied in the aromatization of alcohols. The amount of Zn loading on HZSM-5 (30) was controlled not to exceed 1 wt.%, so that it would not negatively effect on the textural properties of the zeolite.

Table 2-4 represents the different loadings of Zn promoter on the catalyst and their associated acidity. It was noted that by introducing Zn, the catalyst acidity enormously decreased. Moreover, by increasing the wt.% of the metal, the catalyst acidity gradually dropped. The decrease of catalyst acidity would be likely due to the incorporation of bivalent Zn cations in the catalyst framework that would preferentially exchange with strong Bronsted acid sites of HZSM-5 [44]. It was also observed that promoting the catalyst

with Zn had an impact on the acid distribution. Trending the acid properties of the prepared catalysts by NH₃-TPD represented a decline in the number of weak and strong acid sites, but increase in the number of medium acid sites [40].

Table 2- 4 Influence of Zn loading by IE method on the catalyst acidity [40]

Catalyst	Zn loading (wt.%)	S _{BET} (m ² /g _{cat})	Acidity (μmol/g _{cat})
HZSM-5 (30)	0	389.0	373
0.45Zn/HZSM-5	0.45	375.7	290
0.48Zn/HZSM-5	0.48	356.0	287
0.59Zn/HZSM-5	0.59	346.9	255
0.64Zn/HZSM-5	0.64	345.5	192

The conversions of glycerol within all of the evaluated catalysts were complete. However, it was found that incorporating Zn remarkably enhanced the carbon yield of aromatics and decreased the production of paraffins (Fig. 2-3). Catalytic conversion of glycerol over 0.64Zn/HZSM-5 resulted in the highest production of liquid aromatics and the least formation of paraffins. Moreover, by trending the evolution of aromatics distribution versus increasing wt.% loading of Zn, it was observed that selectivity of the reaction toward gasoline-range aromatics, especially toluene, gradually increased from around 18% to 39%.

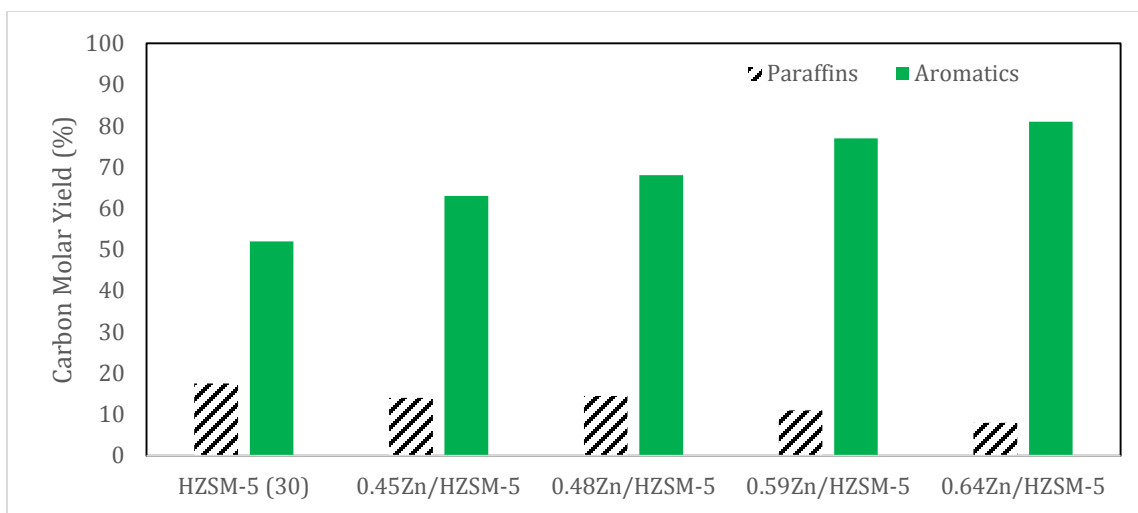


Figure 2- 3 Production of aromatics and paraffins as a function of Zn loading by IE method, operational condition: 400°C, 300 psig, and W/F 3h [40]

Tamiyakul et al. concluded that the enhancement of aromatics production after introducing Zn species to HZSM-5 would be because of two reasons. 1- Exchanging Zn with strong Bronsted acid sites suppressed the hydrogen transfer reaction that would result in the formation of saturated hydrocarbons (paraffins). Hence, this allowed the formation of more olefins that led to higher production of aromatics. 2- The high capacity of Zn cations in the dehydrogenation reactions, facilitated the aromatization reactions.

2.3.2 Two-Bed Configuration of Pd/Zno and HZSM-5 Catalysts

Hoang et al. proposed that converting glycerol to mono-functional oxygenates prior to the favored aromatization mechanism would increase the reaction selectivity to gasoline-range aromatics [39]. To facilitate the first step, Pd/ZnO as a deoxygenation catalyst was placed before HZSM-5. Glycerol catalytic conversion over this two-bed catalyst system was evaluated at 400°C and 2 MPa, and the results were compared to the performance over HZSM-5 single bed catalyst (Table 2-5). The formation of oxygenates as final products

significantly decreased through the two-bed catalytic cracking of glycerol, whereas the selectivity to aromatics increased. Moreover, it was observed that placing the Pd/ZnO catalyst before the zeolite-based catalyst changed the main oxygenate product. Selectivity to propenal, which was the main product over single HZSM-5 catalyst dropped down from 59.4% to 5%. However, selectivity to mono-functional oxygenates such as alcohols and acetaldehyde increased. Even though no formation of aromatics was detected through the catalytic conversion of glycerol over the single-bed deoxygenation catalyst, the two-bed system configuration shifted the distribution of liquid aromatic products. The almost even distribution of aromatics within the range of C₇ to C₁₂ over HZSM-5 catalyst mostly shifted toward C₈-C₉ aromatics over the two-bed configuration.

Table 2- 5 Comparison between the performance of single-bed and two-bed catalysts on glycerol catalytic conversion

Catalyst	Pd/ZnO	HZSM-5	Pd/ZnO + HZSM-5
Conversion (%)	91.7	96.9	99.0
Oxygenates (mol _{carbon} %)			
Propenal	2.9	59.4	5.0
Acetaldehyde	10.4	7.8	22.4
Alcohols	24.7	0.2	33.0
Total	91.7	76.0	63.5
Aromatics (mol _{carbon} %)			
C ₈ Aromatics	0	3.6	11.8
C ₉ Aromatics	0	3.9	11.1
Total	0	20.9	35.5

It was interpreted that separating the catalytic activity for the deoxygenation from oligomerization and cyclization mechanisms directly enhanced the production of gasoline-range aromatics. Unlike the low conversion of propenal over HZSM-5 catalyst to other compounds, propenal could be readily hydrogenated over Pd/ZnO due to the presence of active dehydrogenation metal (Pd) and form oxygenates such as alcohols, ketones, and aldehydes. These mono-functional oxygenates would likely later on undergo solid acid-favored mechanisms including aldol-condensation, oligomerization, and cyclization over HZSM-5 catalyst to form valuable alkyl-aromatics [39].

2.3.3 Catalytic Conversion of Glycerol/Alcohol Mixture

The addition of alcohols to glycerol as feedstock for the catalytic conversion over zeolite-based catalysts was another optimization method that was tested in a few studies. Luo et al. provided a comparison between methanol-to-gasoline (MTG) and methanol-and-glycerol-to-gasoline (MGTG) over ZSM-5 at different temperatures and methanol/glycerol composition ratios [43]. The best catalytic conversion process in terms of producing higher gasoline-range aromatics was found to be for the MGTG process at 500°C with the addition of 10wt.% glycerol in methanol. Introducing 10 wt.% glycerol next to methanol enhanced the formation of liquid aromatics from 11 wt.% to 14.9%, but the catalyst life time dropped by almost 50%. Moreover, it was found that increasing the glycerol to methanol ratio had a negative impact on the production of gasoline-range aromatics and catalyst stability.

In addition to methanol, Jang et al. also evaluated the influence of introducing other alcohols such as ethanol, isopropanol, and isobutanol next to glycerol and compared them to the catalytic conversion of glycerol/water mixture over HZSM-5 (30) catalyst at 400°C [30]. To compare the products, the molar ratio of glycerol to water and glycerol to alcohol

were fixed at 1/12. It was found that with substituting the dilution media from water to alcohols, the carbon yield of total aromatics remarkably increased by 23% on average, which strongly indicated a synergetic effect of glycerol and alcohols toward the formation of aromatics. The distribution of aromatics fraction was also affected by the type of dilution media. It was evaluated that the addition of methanol to glycerol resulted in the highest aromatics fraction for the xylenes (46%) and the least for heavy aromatics (C₁₀ and above). Modifying the H/C_{eff} ratio of the feed was claimed to be the main cause for this significant enhancement. By increasing the H/C_{eff} ratio from 0.67 to 1.90, intermediate products would have higher chance to undergo constructive mechanisms such as aldol-condensation and dealkylation rather than solidifying over HZSM-5 catalyst and decrease the life-time.

To find the effective glycerol/alcohol ratio to utilize the process in terms of aromatics production and maximize the catalyst life-time, another set of experiment with the use of glycerol/methanol and glycerol/ethanol as feeds was also performed [30]. For the both type of alcohols, it was found that increasing the glycerol to alcohol composition ratio decreased the carbon yield of aromatics and increased the catalyst deactivation rate. For instance, increasing the fraction of glycerol from 14.3 wt.% to 40.0 wt.% in the glycerol-ethanol process over HZSM-5 at 400 °C, the carbon yield of total aromatics dropped from 30% to 16% at the end of the catalyst life-time (26 h for 14.3 wt.% glycerol/EtOH and 8 h for 40.0 wt.% glycerol/EtOH). It was interpreted that by increasing the glycerol/alcohol ratio, glycerol oxygenated intermediates would likely block the strong Bronsted acid site, which would lead to the restriction of acid-favored mechanisms such as aldol-condensation. So the carbonization reaction might occur in the catalyst pores and result in fast catalyst deactivation.

2.4 Gasoline-Range Aromatics

Gasoline-range aromatics or light aromatics usually refer to the liquid fraction of aromatic hydrocarbons mostly including benzenes, toluene, xylenes, ethylbenzene, and trimethylbenzenes (TMBs). Although the unlimited addition of aromatics- especially benzene- to gasoline is restricted due to environmental regulations in many regions, light aromatics such as toluene and xylenes are still applied in the gasoline as octane boosters in some areas [45]. For instance in Europe, the finished gasoline is permitted to include aromatics no more than 35% by volume [45]. The finished Japanese premium gasoline contains 22.3 wt.% toluene and 3.9 wt.% 1,2,4 trimethylbenzene as octane boosters. In Chinese regular gasoline also, 2.6 by weight percent m-xylene is added in order to enhance the octane number [46].

Moreover, light aromatics are extensively used in other petrochemical applications and related industries. For instance, toluene is widely being used as a solvent in many applications such as painting, coating, adhesives, and inks [47]. Xylenes are usually clear and colorless aromatic hydrocarbons, which consist of three isomers. They are widely used as solvents in the leather, rubber, and printing industries. Paraxylene is one of the most important isomers of xylenes, which is a raw material in the preparation of polyethylene terephthalate (PET) chips [48]. Finally, TMBs are commonly used as intermediates and precursors in the polymer industry and the production process of materials such as plastics [49].

Chapter 3 Methods and Analytical Procedures

3.1 Experiment Sets

To elaborate the influence of co-processing on the catalytic conversion of glycerol to gasoline-range aromatics over alumina, three different sets of experiments were performed:

- i.* Catalytic co-cracking of four different components of methanol, ethanol, dodecane, and n-hexadecane next to glycerol over alumina at 470°C,
- ii.* Catalytic co-cracking of n-hexadecane next to glycerol over alumina at five different composition ratios at 470 °C,
- iii.* Catalytic co-cracking of n-hexadecane next to glycerol over alumina at four different operational temperatures

For the co-feed type analysis in the set *I*, the selected co-feed composition ratio was 75/25 weight percent glycerol/compound model.

For the set *ii*, the selected n-C₁₆ to glycerol composition ratios were respectively 0/100, 25/75, 50/50, 75/25, and 100/0 weight percent.

For the temperature analysis in the set *iii*, the selected operational temperatures were respectively 400°C, 470°C, 540°C, and 610°C; and the feed composition ratio was 50/50 glycerol/n-hexadecane weight percent.

3.2 Feed

Throughout this study, glycerol, methanol, ethanol, dodecane, and normal hexadecane were used as feed in different experiments. In most of the experiments glycerol was used as the main feed.

3.2.1 Glycerol

Glycerol (purchased from Fisher) was the main feedstock in the all three sets of experiments and was covered in both chapter 4 and 5. Table 3-1 indicates the major physical properties of glycerol [50]. Glycerol in the ambient temperature is very viscous and hardly miscible in hydrocarbons. In order to perform a vapor phase study on glycerol, the operational temperature should be at least above 290°C at atmospheric pressure.

Table 3- 1 Physical properties of pure glycerol

Properties	Glycerol
Chemical Formula	C ₃ H ₈ O ₃
Molecular weight (gr/mol)	92.09
Melting Point (°C)	18.17
Boiling Point (°C)	290
Density @20°C (g/cm³)	1.26
Viscosity @20°C (cP)	1499

3.2.2 Methanol

Methanol (CH_3OH), purchased from Fisher, was used as an alcohol compound model co-feed next to glycerol in Chapter 4. Methanol is completely soluble in glycerol and has a boiling point of 64.70°C at atmospheric pressure.

3.2.3 Ethanol

Ethanol ($\text{C}_2\text{H}_6\text{O}$), purchased from Commercial Alcohols Inc., was also used as an alcohol compound model co-feed next to glycerol in Chapter 4. Ethanol is completely soluble in glycerol and has a boiling point of 78.37°C at atmospheric pressure.

3.2.3 Dodecane

Dodecane ($\text{C}_{12}\text{H}_{26}$), purchased from Acros, was used as a long-chain paraffin compound model co-feed next to glycerol in Chapter 4. The selected dodecane is a mixture of isomers, not soluble in glycerol and has a boiling range of $175\text{-}192^\circ\text{C}$ at atmospheric pressure.

3.2.3 Hexadecane

Hexadecane ($\text{C}_{16}\text{H}_{34}$), purchased from Sigma, was also added as a long-chain paraffin compound model next to glycerol in Chapter 4 and Chapter 5. The content of the selected hexadecane is 99% normal paraffin, not soluble in glycerol and has a boiling point of 286.82°C at atmospheric pressure.

3.3 Catalyst Preparation and Characterization

The alumina catalyst used in this work was prepared from boehmite (purchased

from Sasol). For catalyst matrix preparation, 20g of binder was dissolved in 20g of concentrated HCL. Then, the alumina powder was added into the mixture and distilled water was introduced in drops. The mixture was placed into a water bath at 60-65°C, and it was stirred continuously until distributed evenly. Next, the mixture was introduced into an extruding machine to shape the catalyst that was then dried at the temperature of 38°C overnight and further dried in a muffle oven at 120°C for 2 hours. The dried catalyst was subsequently calcined at 550°C for 5 hours. Finally, the calcined catalyst was crushed and sieved through 40-80 mesh sieves.

Table 3- 2 Catalyst characterization and properties

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)	Acid sites (*10 ⁻² mmol/g)			
				Weak	Medium	Strong	Total
Alumina	152.9	0.5	14.1	14.0	3.9	7.5	25.4

Table 3-2 summarizes the properties of the prepared Al₂O₃ catalyst. The specific surface area, pore volume, and pore size distribution of catalyst were determined by N₂ adsorption at -77K on an Autosorb1-C (Quantachrome Instruments, USA). Prior to measurement, the sample (50-500 mg) was degassed at 300°C. The surface area of the catalyst was calculated using the Brunauer-Emmet-Teller (BET) method. The total pore volume was the volume of nitrogen that was adsorbed under the relative pressure p/p₀ at 0.995. The pore size distribution of catalyst was calculated using the Barrett-Joyner-Halenda (BJH) method. The strength and amount of acidic/alkaline sites on the surface of catalysts was determined by NH₃/CO₂ temperature program desorption (TPD) using a Quantachrome Autosorb 1-C and a Residue Gas Analyzer (RGA-200, Stanford Research Systems Inc., 42 USA). A 100-1000 mg catalyst sample was loaded into a U-shaped quartz tube, which was then placed in a furnace. The catalyst was treated in-situ at 120°C for 1

hour in helium and then was vacuumed for 30 minutes. Next, the catalyst underwent NH_3 or CO_2 adsorption at 120°C for 1 hour, and then physi-desorption at 120°C by helium purging. Finally, the catalyst was heated up to 900°C (at a rate of 10°C per minute) for chemi-desorption. The weak, medium, and strong active sites of the catalyst were assigned to the peak areas of the NH_3 -TPD curves lower than 350°C , between 350 and 500°C , and above 500°C , respectively.

3.4 Experimental Procedure

Catalytic experiments were performed in a gas phase using, fixed bed reactor (quartz tube, 0.8cm inner diameter, and 70cm in length). Fig. 3-1 shows the simplified process flow diagram of the overall reaction system. The system includes two parallel injectors designed to facilitate co-feeding the immiscible samples simultaneously and evenly, a preheating section using a thick layer of quartz wool before the catalyst bed entrance (usually 330 - 340°C inside) to let the immiscible liquid phase feeds vaporize completely and potentially mix well in the gas phase before undergoing reactions, a catalyst bed, a cooling zone maintained at 10°C , and a gas-liquid separator (-15°C iced bath). Gaseous products were collected through water displacement method. To perform the individual catalytic conversion runs, syringe 2 was blocked in place.

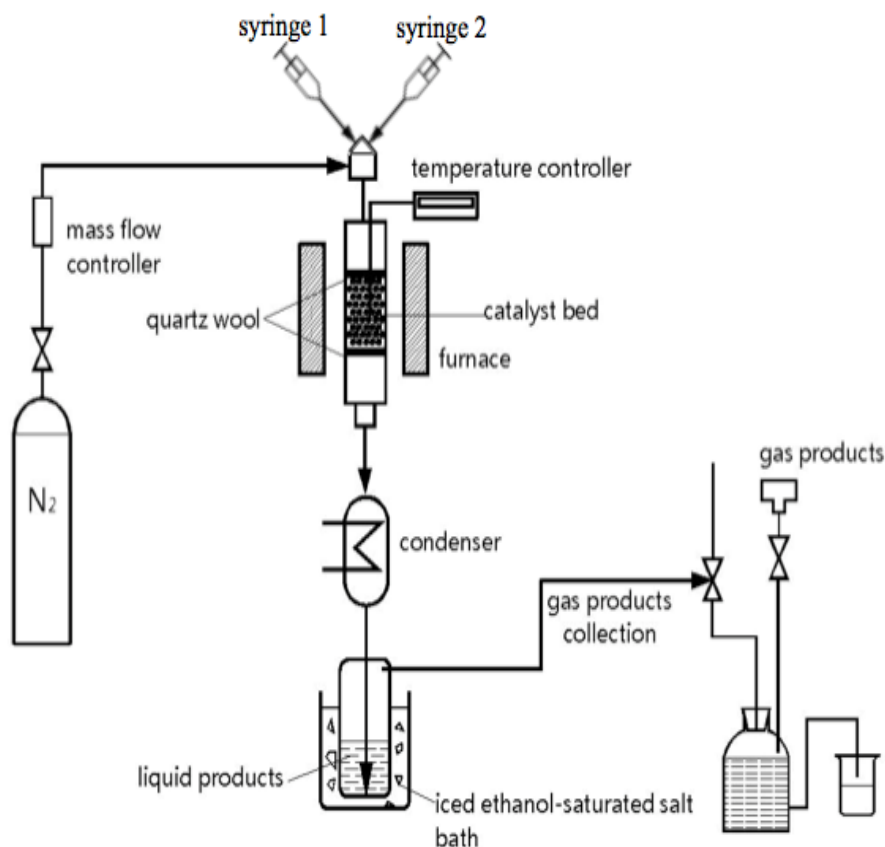


Figure 3- 1 Fixed-bed reactor for glycerol catalytic conversion evaluation

3.3 Product Analysis

In chapters 4 and 5, all three streams of gas, liquid, and solid were evaluated with different scopes. Moreover, to perform the liquid products analysis, the aqueous and organic phases were separated.

3.3.1 Gas Products

Gas analysis performed by two different estimation and accurate methods described in chapters 4 and 5. As the main focus in chapter 4 is on the liquid organic phase, the quantity of formed gas products were estimated using the Ideal Gas Law in the purpose of

comparison between different co-feeding runs [51]. In order to do that, the volume of the gas phase products was calculated via subtracting the carrier gas volume from the overall volume. Then, Ideal Gas Law was applied for the gas products volume assuming the average molecular weight of 40gr/mole to calculate the estimated mass.

In chapter 5, the compositions of inorganic gases, such as CO, CO₂, and H₂, were tested by a combination of a GC (Varian GC-3400) equipped with an Agilent HP-PLOT Q column (19095P-QO4, 30mÅ~0.53mmÅ~40µm), and a Residue Gas Analyzer (GC/RGA). Helium was used as a carrier gas, and the flow rate of helium was 15ml/min. The quality analysis of CO, CO₂, and H₂ in the gas products was determined from the signals of the mass/charge (m/z) ratios: 12, 44, and 2, and the quantity analysis were determined by an external standard method.

Composition of hydrocarbons in the gas products in chapter 5 was determined by gas chromatography with a Flame Ionization Detector (GC/FID, GC-17A), which was equipped with a middle range polarity column (19095P-S25, 50m×0.53mm×15um DF). The temperature program was: 35°C for 2min, 190°C with 10°C/min, and 190°C for 20min. The injection temperature and detector temperature were 60°C and 210°C, respectively. The quality analysis was conducted by standard gas and the quantity analysis was conducted by an external standard method.

Analyzing the gas products from the individual catalytic conversion of glycerol in both chapter 4 and 5 was performed accurately using the latter method.

3.3.2 Liquid Products

Both in chapter 4 and 5, the qualitative chemical compositions of the liquid

products were analyzed by gas chromatography (SHIMADZU GC-17A) coupled with mass spectrometry (SHIMADZU MS-QP5000) (GC/MS, Shimadzu Scientific Instruments, Japan), equipped with an Agilent HP-5MS column. The temperature program was: 60°C (5mins), 180°C (rate: 10°C/min, 5mins), 240°C (rate: 8°C/min, 5mins), and 300°C (rate: 20°C/min, held for 4.5min). The injection and interface temperatures were at 305°C and 320°C, respectively. Full-scan mass spectra were acquired from 30 to 500 m/z at a scan speed of 1000.

The quantitative testing of hydrocarbons in the liquid samples was determined by external standard method using a Varian 450 gas chromatography coupled with an FID, equipped with a non-polar capillary column (Agilent J&WVF-1ms). The temperature program was: 60°C (5mins), 230°C (rate: 7°C/min), and 300°C (rate: 10°C/min, 5mins). The injection and interface temperatures were at 305°C and 320°C, respectively.

Cracking conversion of long-chain paraffin feeds in both chapter 4 and 5 were also determined using the latter gas chromatography machine. However, this parameter was measured by internal standard method. As the internal standard should be very similar but not identical to the analyte [52]. Normal-docosane (C₂₂H₄₆) was selected for both hexadecane and dodecane co-processing runs.

The quantitative analysis of oxygenates in the liquid products was complicated and a full detailed study of oxygenates was not provided. However, a brief elemental study was implemented to evaluate the status of oxygenates. The formed organic phase and aqueous phase were tested separately. The contents of carbon, hydrogen, and oxygen in the aqueous products were tested by LECO CHN-932 elemental analyzer (LECO Corporation, MI, US). Aqueous samples were combusted in an oxygen atmosphere at 1150°C. The

responses to the contents of carbon and hydrogen were calibrated by the standards, whereas the contents of oxygen were calculated by subtraction. From all of the tested samples it was confirmed that content of carbon is quite insignificant (<1%). Therefore, it is assumed that in chapters 4, 5, and 6, “aqueous phase” mainly refers to H₂O.

To facilitate in the study of the influence of co-processing hexadecane on the glycerol reaction pathway in chapter 5, the content of oxygen in the liquid organic phase was also determined. These samples were tested using the same elemental analyzer through the discussed subtraction method.

3.3.3 Solid Product

The solid products from the experiments run in chapters 4 and 5 (carbon deposit on the spent catalyst) were firstly analyzed by LECO CHN-932 elemental analyzer as well in order to determine the carbon and hydrogen content. However, the content of oxygen could not be evaluated in the solid products as the catalyst matrix also includes oxygen atoms. Later on, solid products were individually mixed evenly and samples were taken from them to burn in the muffle oven for 4 hours at 550°C to calculate the total solid products weight fraction.

3.4 Calculation Procedure

To make comparative results in chapter 4 and 5, calculations were completed to evaluate both phase weight fraction and carbon molar fraction of the product streams. Through quantitative measurement of products, yield (Y_i), selectivity (S_i), and aromatics carbon fraction (F_i) of species i are calculated as follows:

$$Y_i = \frac{\text{mass of species } i \text{ (g)}}{\text{mass of feed (g)}} \times 100 \text{ wt. \%}$$

$$S_i = \frac{(\text{mole of species } i) \times (\text{number of carbon atom in species } i)}{(\text{mole} \times \text{number of carbon atom}) \text{ of converted feed}} \times 100\%$$

$$F_i = \frac{\text{Selectivity of aromatic species } i}{\text{Total selectivity of aromatics}} \times 100\%$$

To study the influence of co-feeding hexadecane on glycerol cracking performance more exclusively, yield and selectivity based on 1 unit of glycerol (\bar{Y}_i and \bar{S}_i) are defined as follows:

$$\bar{Y}_i = \frac{\text{mass of species } i \text{ (g)}}{\text{mass of fed glycerol (g)}} \times 100 \text{ wt. \%}$$

$$\bar{S}_i = \frac{(\text{mole of species } i) \times (\text{number of carbon atom in species } i)}{(\text{mole} \times \text{number of carbon atom}) \text{ of converted glycerol}} \times 100\%$$

To calculate the selectivity of hydrogen (H_2), the “number of carbon atom” is replaced by the “number of hydrogen atom” in the mentioned equations.

The integrated effective H/C ratio of the glycerol-alcohol runs in chapter 4 is also calculated using:

$$\overline{H/C}_{eff} = \frac{\frac{H}{C} \times \text{mole of glycerol} + \frac{H}{C} \times \text{mole of alcohol}}{(\text{mole of glycerol} + \text{mole of alcohol})} \times 100\%$$

Chapter 4- Co-processing Glycerol and Proton-Donor Species to Gasoline-Range Aromatics over Alumina

4.1 Scope of Work

To study the effect of co-processing on the catalytic conversion of glycerol to gasoline-range aromatics over alumina, individual catalytic cracking of glycerol was studied first. Later on, co-feeding runs were performed by introducing alcohols (methanol and ethanol) and long-chain paraffin (dodecane and n-hexadecane) next to glycerol, under identical operational conditions. In order to discuss the effect of co-feeding on the aromatic products, and more specifically gasoline-range aromatics, results derived from different co-feeding experiments are rigorously compared.

4.2 Catalytic Conversion of Glycerol over Alumina

Individual catalytic conversion of glycerol over alumina was studied at 470°C using 45 ml/min inert carrier gas at 20 psig. Even though glycerol is a viscous compound, the attempt of slow injecting of the feed (~1.8 gr in 180 secs) to the fixed-bed reactor was successful.

4.2.1 Mass Analyses

Table 4-1 indicates the results derived from the catalytic cracking of glycerol over alumina at 470°C. During the product analysis, glycerol was not detected in the obtained aqueous and organic products. Hence, it is concluded that glycerol catalytic conversion was close to 100% (>99%). The liquid phase stream had the highest yield (wt.%) among

the products. However, Fig. 4-1 details that a very small fraction of the liquid product was in the organic phase and about 88% of it was formed in the aqueous phase. Completing the elemental analysis for the aqueous phase product accounted that the carbon content in this stream was totally negligible (Less than 1%). This finding indicates that almost the entire formed aqueous phase just includes H₂O. Therefore, it is acceptable to claim that 20.6 wt.% of carbon deposit was considerably high since potentially the majority of carbonaceous products are concentrated there.

Table 4- 1 mass distribution in the individual catalytic conversion of glycerol at 470°C

Experiment	Glycerol Conversion (%)	Carbon Deposit (wt.%)	Liquid (wt.%)	Gas (wt.%)
Glycerol	100	20.60	56.54	17.93

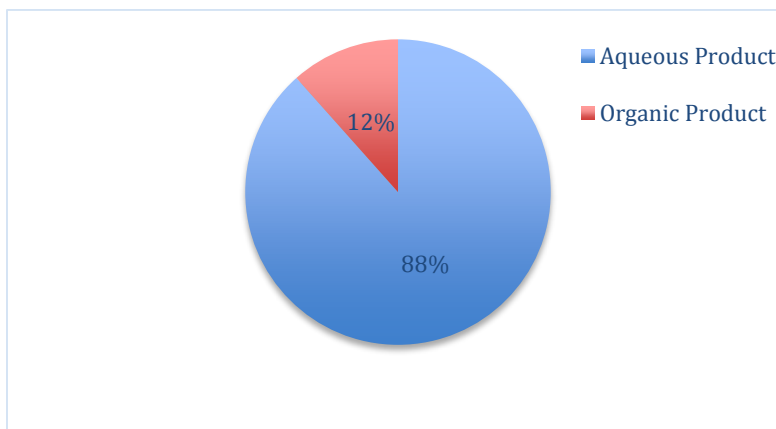


Figure 4- 1 organic product fraction in the liquid phase of the 100% glycerol run

4.2.2 Product Distribution

Selectivity to different products is detailed in Fig. 4-2. The formed carbon deposit on the catalyst surface had significantly the highest selectivity among all of the products

and constituted 73% of the carbon content. On the other hand, even though the formed organic phase stream primarily included aromatics (>97%), the overall carbon molar selectivity to aromatic products with 17.3% was relatively low. CO₂+CO had the highest selectivity among the gaseous streams, which could be attributed to the deoxygenation of glycerol through both decarbonylation and decarboxylation reactions.

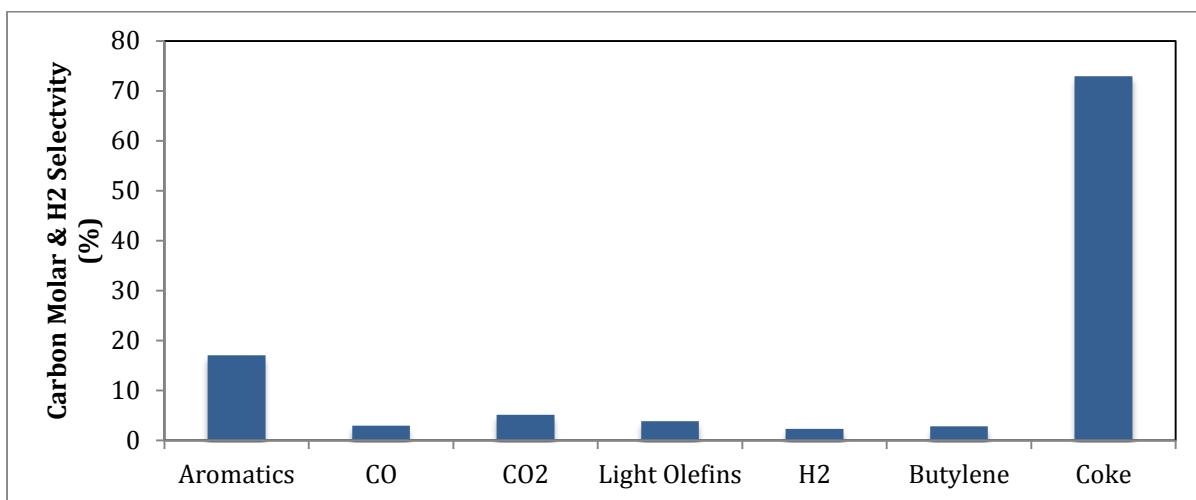


Figure 4- 2 product distribution of glycerol catalytic conversion over alumina at 470°C

4.2.3 Distribution of formed Aromatic products

Catalytic conversion of glycerol over alumina at 470°C was highly reluctant to form light aromatics and mostly created heavy undesired cyclic compounds. Fig. 4-3 details the carbon fraction of produced aromatics. Comparing to the produced aromatics with 10, 11, or 12 carbons (29, 34, and 26% respectively), the fractions of produced toluene, xylenes, and trimethylbenzenes (TMBs) were remarkably small, and there was almost no formed benzene. Among all of the formed compounds, 3-methyl-1H-indene (C₁₀H₁₀) had the

highest selectivity, which would evidence the formation of large molecules in the catalyst pores and the difficulty of organic products to leave the catalyst surface.

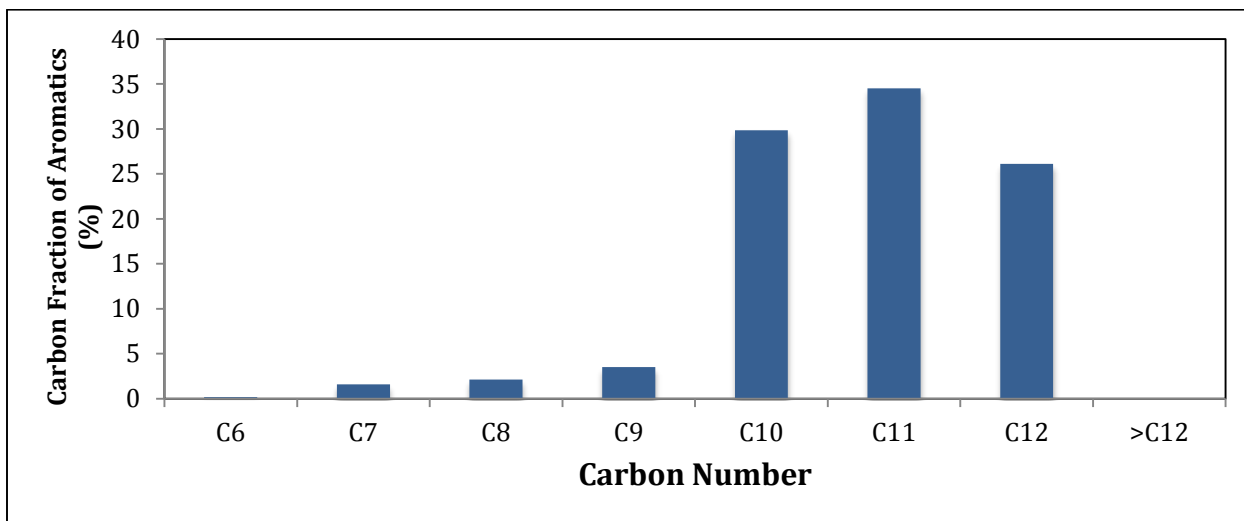


Figure 4- 3 Aromatic products distribution of glycerol catalytic conversion over alumina at 470°C

4.2.4 General Overview of Glycerol Catalytic Conversion over Alumina

A relatively small organic phase yield, which mainly includes heavy aromatics, could also evidence that the majority of injected carbon content in the glycerol was converted to the larger molecules and solidified on the catalyst surface. High selectivity to the carbon deposit might be due to the severe oligomerization reactions of glycerol and its intermediates occurring on the catalyst and the blockage of the active acid sites. It was reported in several studies that the catalyst porosity and acidity have immense impacts on the reaction pathway of catalytic conversion restricting carbonaceous deposit formation [28, 53, 54]. Large pore size may favor diffusion of the relatively large oxygenated intermediates to the catalyst and lead to form coke. Concerning the catalyst acid site type,

due to the steric constraints, the Lewis acid site in the catalyst is more likely to interact with terminal –OH groups in the glycerol and remove it as water [27].

Fig. 4-4 shows the major proceeding mechanism of glycerol catalytic conversion towards large molecules over relatively large pore size Lewis acid catalyst in comparatively high temperatures. After interacting the Lewis acid site with the terminal -OH group and removing water, the dehydrated intermediate is then tautomerized to yield hydroxyacetone [27]. Lacking the presence of available proton-donor acid sites (Bronsted site) or any other proton-donor intermediates in the process causes hydroxyacetone to undergo self-oligomerization reactions under the high thermal condition. So the required proton to remove the second -OH group is provided by the same intermediate. Consequently, this self-oligomerization mechanism may continue and lead to excessive dehydration and form large molecules with low H/C_{eff} ratio, which may carbonize on the catalyst surface. Moreover, the presence of formed water could also adversely affect the acidity and stability of the catalyst [40].

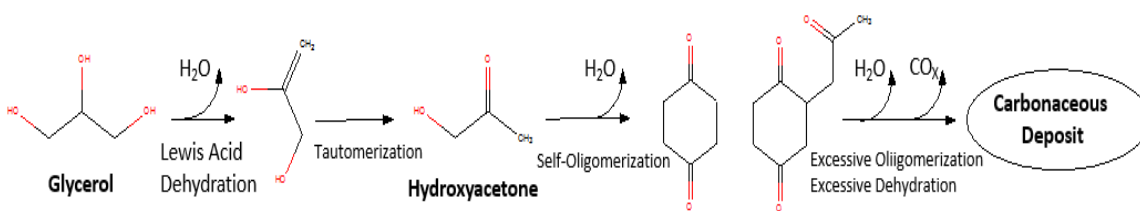


Figure 4- 4 proposed reaction pathway for the individual catalytic conversion of glycerol over alumina at 470°C

Glycerol over Lewis acid catalysts, such as alumina, is very active, and it almost completely converts to other products at 470°C. However, selectivity of the conversion reactions to the desirable products is not satisfactory. Significantly high carbon deposit formation on the catalyst surface and low organic phase production are the main obstacles

of glycerol catalytic conversion over alumina. Moreover, individual catalytic conversion of glycerol over alumina is noticeably inefficient in gasoline-range aromatics production.

4.3 Co-Catalytic Conversion of Glycerol and Alcohols over Alumina

With the purpose of enhancing the performance of glycerol catalytic conversion over alumina at 470°C, methanol and ethanol were co-fed next to glycerol. Methanol and ethanol are so-called industrial feedstocks selected as compound models for alcohols, and H/C_{eff} ratio for them is 2.

To keep glycerol as the major feedstock, 25 wt.% of the total injected feed was alcohol and the rest was glycerol. In order to study the results, the focus was mostly on the potential changes from the drawbacks of individual glycerol catalytic conversion, such as high carbon deposit, high aqueous phase, low organics, and low gasoline-range aromatics production.

4.3.1 Mass Analysis

Mass distribution of 75/25 wt.% glycerol/alcohol products are shown in Table 4-2. As per discussion in section 4.2.1, glycerol catalytic conversion is considered to be complete. Moreover, based on the findings from liquid qualitative analysis (no detected ethanol or methanol in the results), it is concluded that both methanol and ethanol have 100% conversion to products in the process. Comparing to the individual catalytic conversion of glycerol, the quantity of liquid phase products in the glycerol/MeOH increased by 5%, but there was no significant change in the run of glycerol/EtOH. The most notable change in both experiments was the improvement of organic product fraction

in the liquid phase. Fig. 4-5 indicates that by co-feeding the alcohol next to glycerol, the organic phase fraction in the liquid phase enhanced by 12-19 wt.%. A decrease in carbon deposit formation and a slight increase in gas products were also observed in the co-processing runs.

Table 4- 2 Mass distribution of products in the glycerol-alcohol runs

Experiment	Glycerol Conversion (%)	Co-feed Conversion (%)	Carbon Deposit (wt.%)	Liquid (wt.%)	Gas* (wt.%)
Glycerol-MeOH	100	100	12.21	61.46	19.95
Glycerol-EtOH	100	100	11.86	56.32	23.16

*Gas yield is estimated through Ideal Gas rule. Refer to section 3.3.1 for more details.

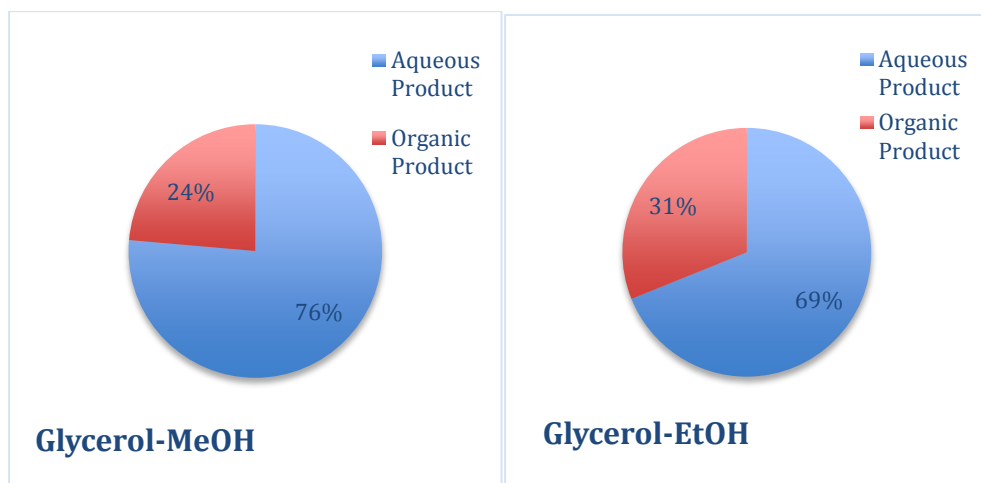


Figure 4- 5 Organic product fraction in the liquid phase of glycerol-alcohol runs

4.3.2 Product Distribution

Selectivity to aromatics and to coke substantially changes after introducing alcohols next to glycerol over alumina at 470°C. Table 4-3 indicates that selectivity to aromatic

products (desired product) rose by 18% in the 75/25 wt.% glycerol-MeOH run. Moreover, the tendency of carbon deposit formation on the alumina surface (undesired product) considerably dropped. Trending this evolution clearly confirms that there is a synergetic effect between glycerol and alcohols toward forming value-added products.

Table 4- 3 Distribution of selectivity to desired and undesired products in the glycerol-alcohol runs

Experiment	Aromatics Selectivity (%)	Coke Selectivity (%)
Glycerol-MeOH	35.08	58.97
Glycerol-EtOH	33.38	57.93

Co-processing methanol next to glycerol resulted in slightly higher aromatics selectivity. However, in terms of co-feeding performance evaluation it is not quite convincing to claim methanol is more efficient than ethanol since the latter resulted in higher liquid organic products.

4.3.3 The Distribution of Aromatic Products

Introducing alcohols next to glycerol also influenced the distribution of the produced aromatic compounds. Adding 25 wt.% methanol next to 75 wt.% glycerol over alumina at 470 °C significantly enhanced the production of trimethylbenzenes and suppressed the formation of heavy aromatics with 11 carbons or more (Fig. 4-6 (a)). Moreover, increase in the formation of xylenes was also noticeable in the co-processing of glycerol and methanol.

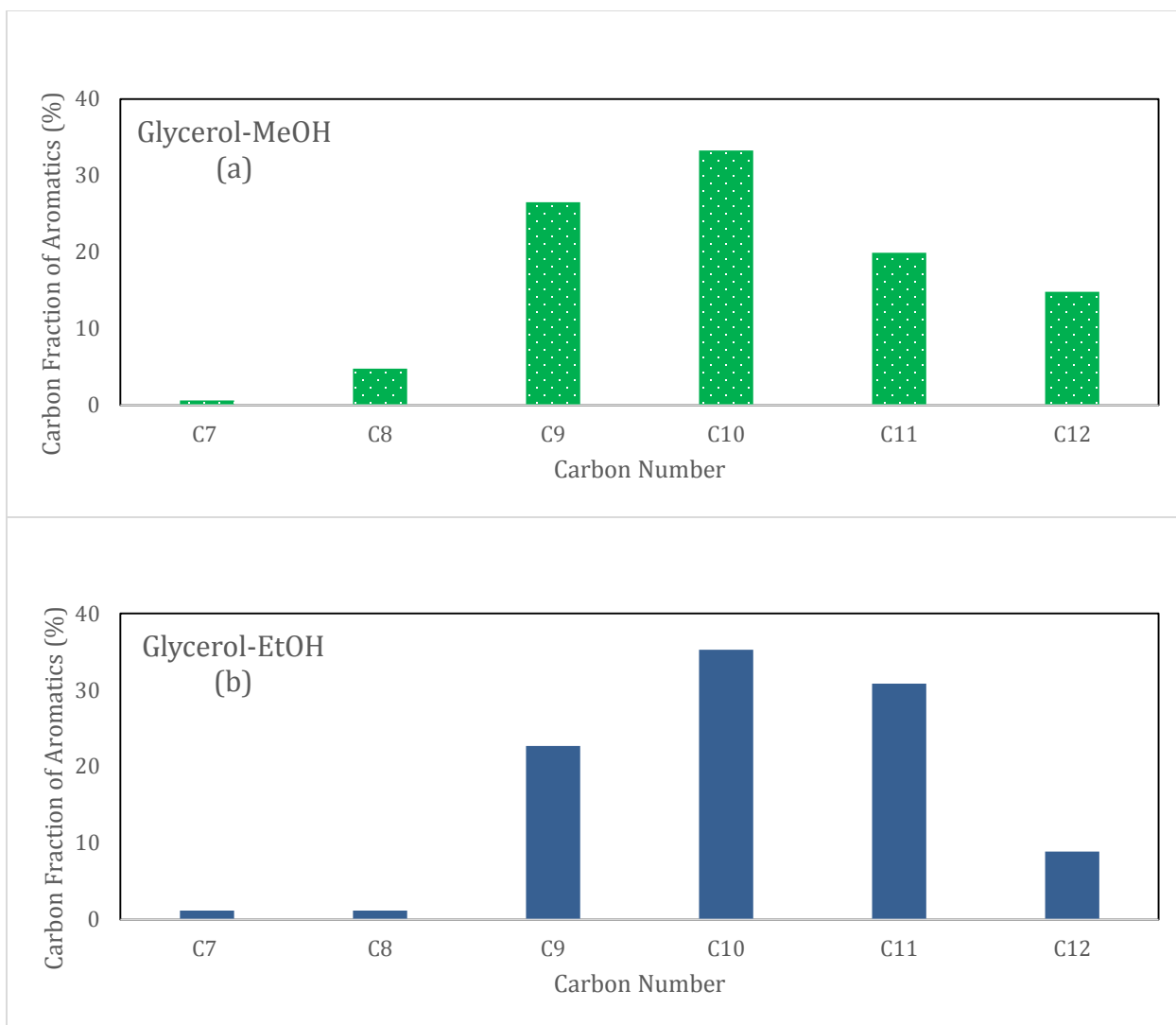


Figure 4- 6 Aromatic products distribution after introducing 25% (a) methanol and (b) ethanol next to glycerol over alumina at 470°C

In comparison to the co-feeding of methanol next to glycerol, adding ethanol was less efficient in terms of gasoline-range aromatics production. Fig. 4-6 (b) accounts that even though selectivity to TMBs increased by 19.6%, there was no significant change in the xylenes production and the formation of undesired aromatic compounds such as C₁₀ and C₁₁ fractions are still relatively as high as individual catalytic conversion of glycerol.

4.3.4 Influence of Co-feeding Alcohols on Glycerol Catalytic Conversion Mechanism over Alumina

Introducing 25 wt.% alcohol next to 75 wt.% glycerol improved the performance of glycerol catalytic conversion over alumina at 470°C. Selectivity to aromatics drastically increased and the tendency to form carbon deposit dropped. Moreover, rise in the formation of trimethylbenzenes was the most noticeable change in the aromatic compounds distribution.

Effective H/C ratio of glycerol is 0.67, and this ratio is 2 for both methanol and ethanol. Accordingly, with the selected 1.04 glycerol-methanol molar ratio and 1.50 glycerol-ethanol molar ratio (75/25 weight percent), the $\overline{H/C}_{\text{eff}}$ ratio is 1.32 and 1.20 respectively.

Modifying the effective H/C ratio in the feedstock would be a preliminary factor for the evolution of products stream after co-feeding methanol and ethanol. Usually when compounds with an effective H/C ratio below 2 are applied as a feedstock, catalyst deactivation is fast due to coking of the catalyst [28]. Increase in the $\overline{H/C}_{\text{eff}}$ ratio of the feed after introducing alcohols to the process would be a leading reason in the rise of selectivity to aromatic products and decrease in coke formation. On the other hand, the higher tendency of glycerol-MeOH catalytic conversion to form lighter aromatics rather than co-feeding glycerol/EtOH could be also explained by the higher effective H/C ratio of the first run.

Improving in the selectivity of aromatic products after introducing alcohols to process would be the result of the increase in the acid-catalyzed (Lewis acid) favored oligomerization reactions such as aldol condensation [30]. Aldol condensation is a Lewis

acid catalyzed favored reaction that likely occurs between an enol or an enolate ion and a carbonyl compound to form β -hydroxyaldehyde [55]. As discussed earlier in section 4-2, glycerol is very active over Lewis acid alumina catalyst and easily dehydrates to hydroxyacetone. In the presence of alcohols (potential enol compounds), this intermediate (potential carbonyl compound) has more opportunity to reach other reactive intermediates with higher effective H/C ratio and form lighter molecules (potential aldol-products) that can leave the catalyst pores more easily.

Even though co-feeding alcohols rises the selectivity to aromatic products, the formation of gasoline-range aromatic compounds is still poor (only increase in C₉ fraction). This finding is aligned with the study completed by Jang et al [30]. Oligomerization reactions such as aldol condensation could be possibly followed by dealkylation reactions to form lighter aromatics including toluene and xylenes. However, it is generally accepted that dealkylation reactions are facilitated by the presence of Bronsted acid sites or proton-donors in the process [56]. Since the process was studied over alumina (Lewis acid catalyst) and alcohols in the excess of glycerol are not active proton-donors, dealkylation reactions would not proceed favorably. However, slight increase in xylenes production in the presence of methanol instead of ethanol likely indicates that the dealkylation step would be more favored to proceed in the glycerol-methanol run than the glycerol-ethanol one.

4.4 Co-Catalytic Conversion of Glycerol and Long-Chain Paraffin over Alumina

The second type of co-feed added next to glycerol in order to improve the performance of glycerol to aromatics catalytic conversion over alumina at 470°C, was

long-chain paraffin. Dodecane and n-hexadecane are selected as compound models for alcohols, and their H/C_{eff} ratios for them are 2.16 and 2.12, respectively.

To keep the glycerol as the major feedstock and to compare the results with the first type of co-processing, 25 wt.% of the total injected feed was long-chain paraffin and the rest was glycerol. Similar to section 4.3, the focus was mostly made on the changes from the drawbacks of individual glycerol catalytic conversion such as high carbon deposit, high aqueous phase, low organics, and low gasoline-range aromatics production.

4.4.1 Mass Analysis

Mass distribution of 75/25 wt.% glycerol/long-chain paraffin products are shown in Table 4-4. Catalytic conversion of glycerol was complete. However, cracking conversion of both dodecane and n-C₁₆ was relatively small. The leading factors for this phenomenon would be the low activity of alkanes over alumina (Lewis acid catalyst) and the mild operational temperature. Industrial catalytic cracking of alkanes are usually performed over zeolite-based catalysts, which include both Lewis and Bronsted acid sites[57]During the catalytic cracking process, Lewis acid sites are active in the initiation step and Bronsted acid sites facilitate the propagation step[58]. Hence, lack of Bronsted acid sites on the catalyst would likely lead to the low cracking conversion of the selected alkanes.

The other triggering reason of low cracking conversion of the selected alkanes would be the extensive presence of glycerol and its intermediates on the catalyst acid sites. Blockage of pores with the carbonized compounds on the catalyst surface might prevent the alkanes from reaching the active sites. However, the calculation of cracking conversion through internal standard method shows that normal-hexadecane has higher conversion

(%) than dodecane. In identical operational parameters, alkanes with longer chains, due to the increase of number of crackable bonds and the higher adsorption rate constant on the catalyst, have higher cracking activity than alkanes with shorter chains [57].

Table 4- 4 Mass distribution of products in the glycerol-long chain paraffin runs

Experiment	Glycerol Conversion (%)	Co-feed Conversion (%)	Carbon Deposit (wt.%)	Liquid (wt.%)	Gas* (wt.%)
Glycerol-Dodecane	100	9.63	17.51	62.48	13.96
Glycerol-Hexadecane	100	12.29	18.30	70.45	13.08

*Gas yield is estimated through Ideal Gas rule. Refer to section 3.3.1 for more details.

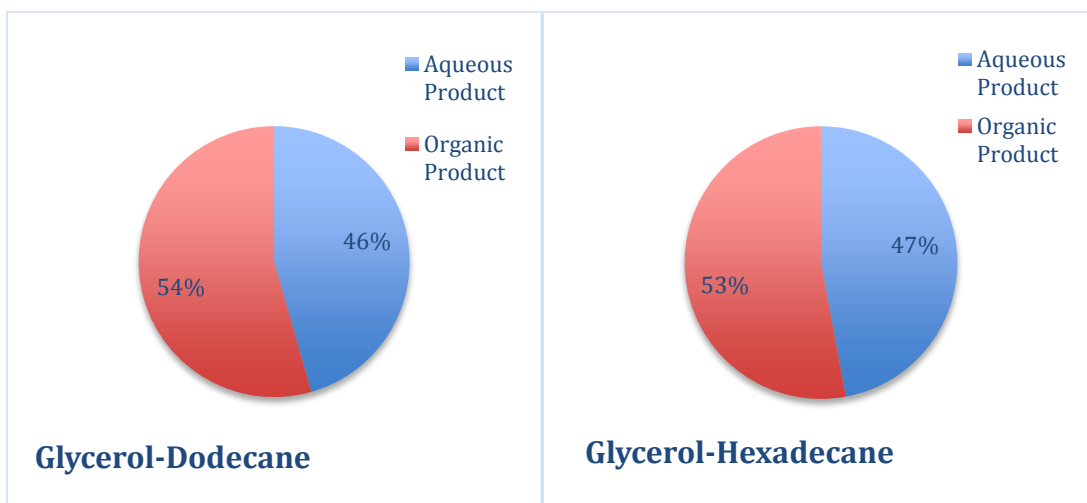


Figure 4- 7 Organic product fraction in the liquid phase of glycerol-long chain paraffin runs

Comparing to the individual catalytic conversion of glycerol, the quantity of liquid phase products in the glycerol-dodecane and glycerol-hexadecane runs increased by 6.1% and 13.9% respectively. Organic phase fraction in the liquid products significantly rose after introducing the alkanes next to glycerol. Fig. 4-7 indicates that in both 75/25

wt.% glycerol/dodecane and glycerol/n-C₁₆, the organic phase products fraction exceeded 50%.

4.3.2 Product Distribution

After introducing the paraffin compounds next to glycerol over alumina at 470°C, selectivity to aromatics increased and the reaction tendency to form coke remarkably dropped. Taking the results of the individual catalytic conversion of glycerol into consideration, the addition of 25 wt.% dodecane or n-C_{16m} clearly creates a constructive modification on the glycerol to aromatics mechanism.

Table 4-5 shows the distribution of the carbon content between the desired and undesired products. Selectivity to aromatics in both runs was enhanced by more than 23%. Moreover, the process tendency to form carbon deposit on the catalyst surface also dropped by around 15% in the glycerol-dodecane run and 20% in the glycerol-hexadecane experiment.

Table 4- 5 Distribution of selectivity to desired and undesired products in the glycerol-long chain paraffin runs

Experiment	Aromatics Selectivity (%)	Coke Selectivity (%)
Glycerol-Dodecane	40.00	55.17
Glycerol-Hexadecane	42.80	50.44

In terms of increasing the desired product and suppressing the coke formation on the catalyst surface, introducing n-C₁₆ next to glycerol had a higher efficiency. This outcome might be due to the longer chain of hexadecane comparing to the 12-carbon chain dodecane. As it was discussed earlier, alkanes with longer chain have higher cracking

conversion. Therefore, under the same condition, n-C₁₆ is more inclined to donate more intermediates to the glycerol and its intermediates to form aromatic compounds.

4.3.3 The Distribution of Aromatic Products

Introducing long-chain paraffin next to glycerol was very effective in enhancing the formation of gasoline-range aromatic compounds. The biggest impact of this co-feeding would be the increase of toluene and xylenes production. Fig. 4-8 (a) indicates that adding 25 wt.% dodecane next to 75 wt.% glycerol over alumina at 470°C boosted the production of xylenes by approximately 16%, and the fraction of toluene rose from 1.6% to 11.1%. On the other hand, tendency to formation of large aromatic compounds also drastically decreased. The fraction of aromatic compounds with 10 and more carbons dropped by 39.6%.

Trending the evolution of aromatic compounds distribution after co-processing glycerol and hexadecane in Fig. 4-8 (b) accounts that the changes are pretty similar to the ones in the glycerol-dodecane run. However, in the glycerol-hexadecane run, selectivity to TMBs is higher by around 5%. The fraction of large aromatic compounds in this run also dropped by 40.5%.

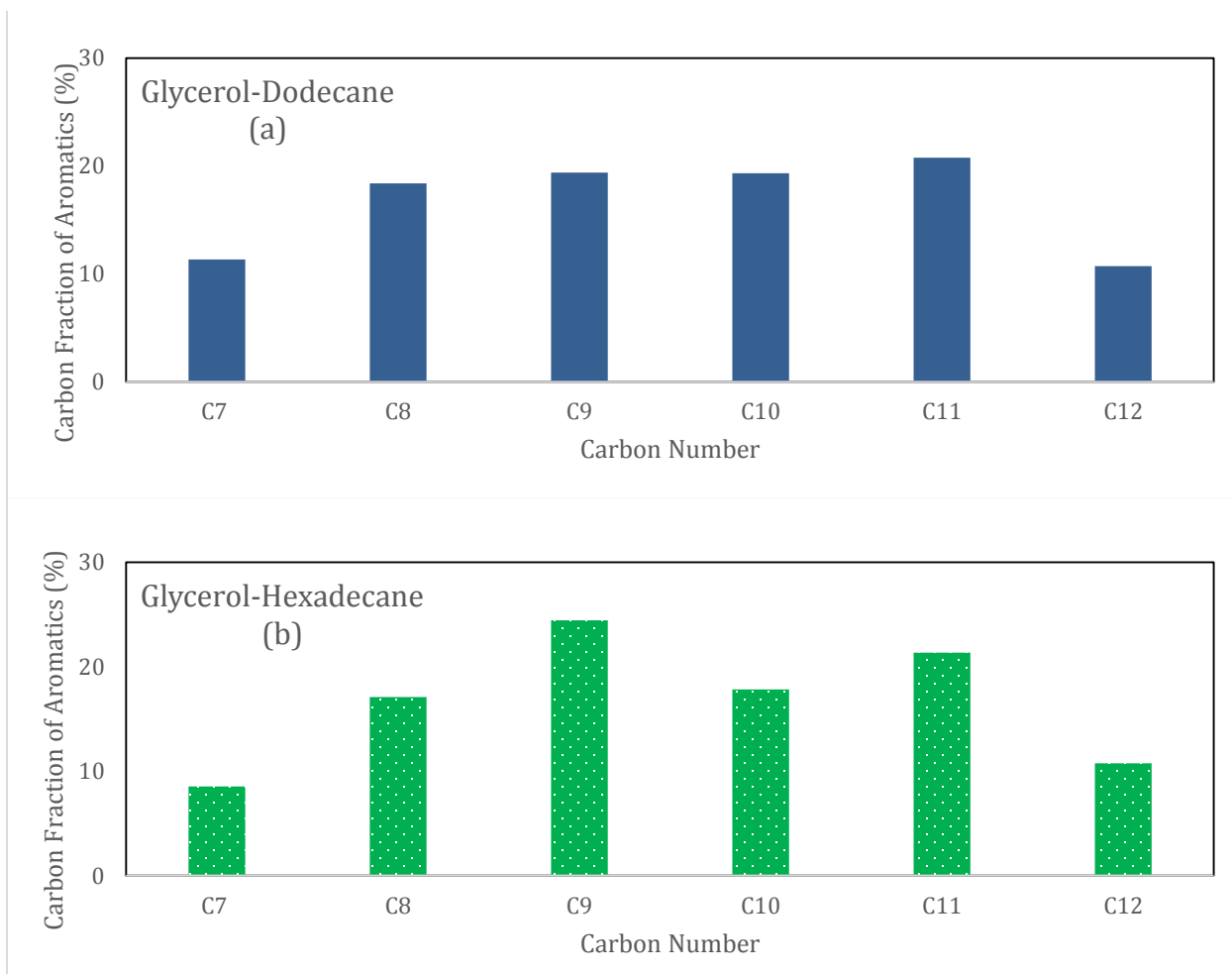


Figure 4- 8 Aromatic products distribution after introducing 25% (a) dodecane and (b) n-C16 next to glycerol over alumina at 470°C

4.3.4 Influence of Co-feeding Long-Chain Paraffin on Glycerol Catalytic Conversion Mechanism over Alumina

Co-feeding 25 wt.% long-chain paraffin next to 75 wt.% glycerol significantly improved the overall performance of glycerol catalytic conversion over alumina at 470°C to value-added products. Suppressing the formation of undesired streams such as coke deposit and aqueous phase product, increasing the selectivity to aromatics, and enhancing

the formation of gasoline-range aromatics are the most noticeable changes of introducing hexadecane next to the main feed.

Even though dodecane and n-hexadecane have considerably high effective H/C ratio, it is not reasonable to calculate the integrated H/C_{eff} ratio in the inlet line since:

- Paraffin and glycerol are not miscible in the liquid phase,
- Glycerol is in the group of oxygenates, but paraffin is a hydrocarbon,
- Paraffin is highly unlikely to directly react with glycerol, and
- Catalytic conversion capability of the selected paraffin and glycerol is not in a same range.

Hence, it is concluded that direct performance evaluation of different glycerol-long chain paraffin runs depend on the cracking conversion capability of the alkane, under the same operational parameters. Comparing to dodecane, n-hexadecane had slightly higher cracking conversion. So, it would likely provide more opportunities for glycerol intermediates to undergo desired reactions, which lead to gasoline-range products.

The co-processed alkanes would affect the glycerol catalytic conversion in two potential ways:

1. Contribution in dealkylation and protonization mechanisms of the oligomerized products and large aromatic compounds
2. Direct reaction between glycerol intermediates and long-chain paraffin cracking intermediates to form aromatic compounds, more specifically gasoline-range ones

Introducing long-chain paraffin next to glycerol enhanced the overall aromatics selectivity and also gasoline-range aromatic compounds. Similar to co-feeding alcohols, long-chain paraffin can also introduce intermediates such as reactive olefins to the process

that might lead to enhance the oligomerization and condensation reactions. Increase in the probability of the described mechanism would suppress the excessive self-oligomerization and solidification of glycerol intermediates on the catalyst surface and boost the formation of liquid phase aromatic compounds. Moreover, it is reported that Lewis acid sites on alumina supports the hydrogenation activity [59]. The formed proton on the catalyst from catalytic conversion of the alkane would likely improve the dealkylation step after oligomerization and condensation reactions. Hence, large aromatic compounds such as C₁₂ fraction would dealkylate and convert to lighter aromatic products such as xylenes.

On the other hand, the introduced intermediates through catalytic conversion of hexadecane or dodecane can also directly undergo Lewis-acid favored reactions with glycerol intermediates over alumina, resulting in the formation of gasoline-range aromatic compounds. For instance, the produced alkenes as the intermediates of long-chain paraffin cracking conversion, before turning into more stable products including lighter alkanes, would likely react with dehydrated intermediates of glycerol through various cyclization mechanisms such as Diels-Alder and Ene processes [28]. Therefore, these mechanisms would facilitate the stabilization of glycerol intermediates via formation of lighter aromatic prior to the occurrence of excessive carbonization on the catalyst surface. Fig. 4-9 represents a simplified model of the potential influence of co-processing long-chain paraffin on glycerol reaction pathway over alumina.

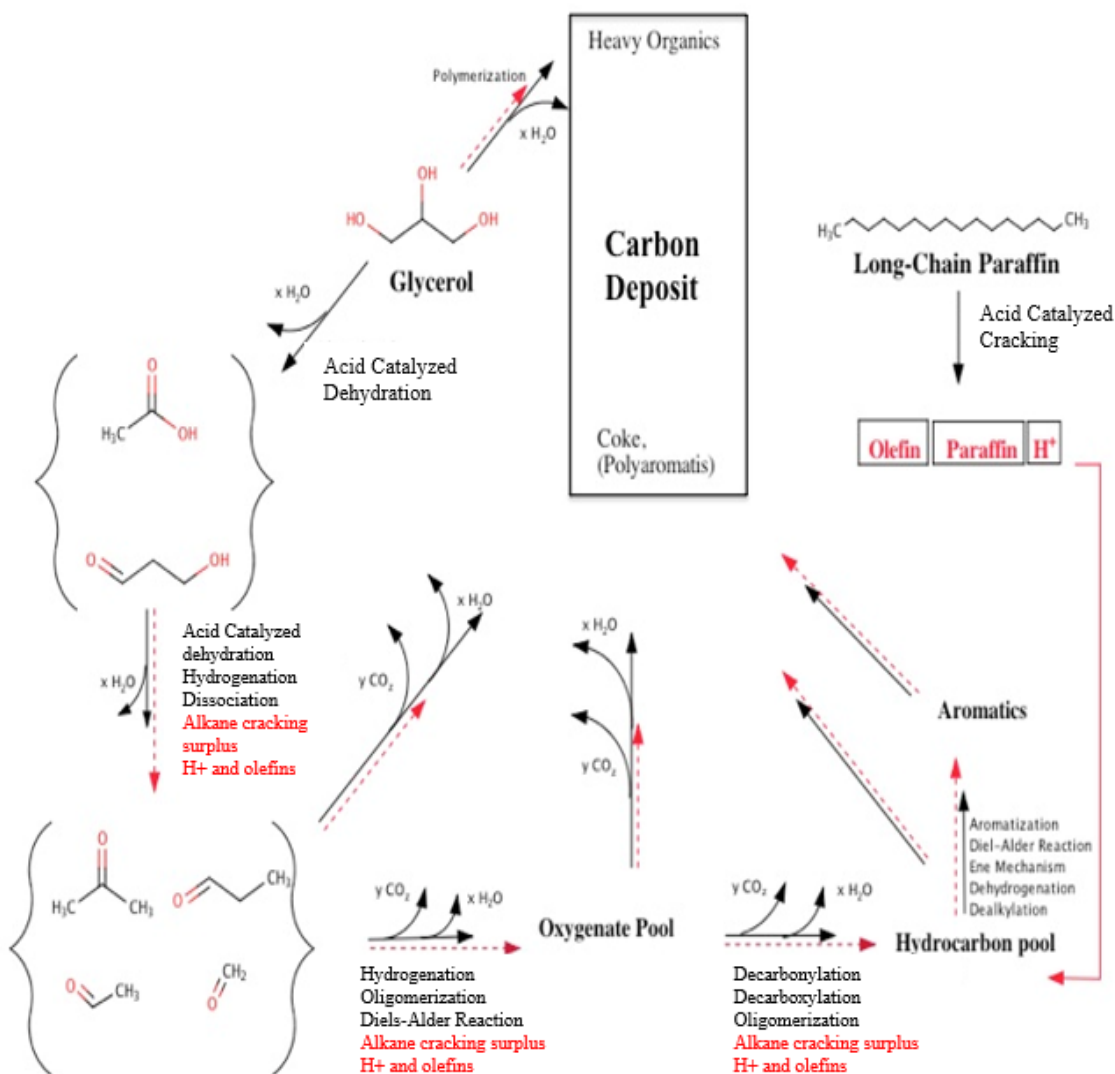


Figure 4- 9 Simplified influence of co-processing long-chain paraffin on the reaction

4.4 Conclusion

Introducing a co-feed enhanced the overall performance of glycerol catalytic conversion over alumina toward aromatic compounds production at 470°C. Glycerol was reactive over alumina and the catalytic conversion was complete. However, individual catalytic conversion of glycerol was very poor in liquid aromatic compounds production

and excessively led to formation of carbon deposit on the catalyst surface. Self-oligomerization was probably the major proceeding mechanism in case of pure glycerol catalytic conversion. In the absence of reactive proton-donors and hydrogen-efficient intermediates, hydroxyacetone, as a glycerol dehydrated intermediate over Lewis acid site, would likely reach each other to remove the contained –OH groups and stabilize. Hence, the mechanism will lead to high carbon deposit and aqueous phase formation, but will be inefficient in organic phase production.

Unlike in the previous studies regarding the co-processing of glycerol, this was focused in keeping glycerol as the major feedstock. 25 wt.% alcohols or long-chain paraffin was added next to glycerol as a minor feed. Introducing alcohols in the process significantly increased the selectivity to aromatic compounds and suppressed the formation of carbon deposit on the catalyst surface. However, the major drawback of co-feeding alcohols was relatively inadequate selectivity to gasoline-range aromatics. It was proposed that introducing alcohols to the process influenced the glycerol catalytic conversion mechanism by increasing the integrated effective H/C ratio, which would likely lead to enhance the oligomerization and aldol condensation reactions over alumina. But, reactions to favor the formation of lighter aromatic compounds, such as dealkylation step are limited. It was observed that methanol has relatively higher efficiency, especially in forming gasoline-range aromatics, which could be due to the higher H/C_{eff} ratio of the glycerol-methanol run over glycerol-ethanol one.

Introducing long-chain paraffins significantly influenced the catalytic conversion of glycerol over alumina at 470°C. Even though the selected alkanes had relatively low cracking conversion, co-processing them next to glycerol significantly increased the

production of gasoline-range aromatic compounds and noticeably dropped the tendency to form undesired streams.

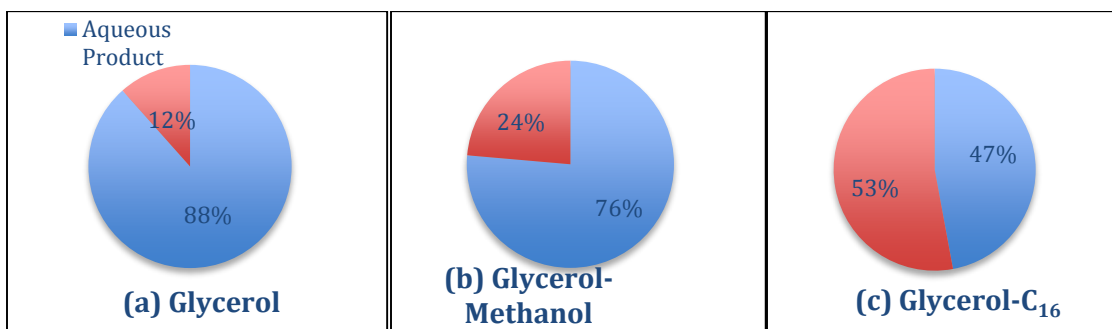


Figure 4- 10 Comparison of liquid phase distribution before and after co-feeding

Table 4- 6 Selectivity to desired and undesired products before and after co-feeding

Experiment	Aromatics Selectivity (%)	Coke Selectivity (%)
Glycerol	17.36	73.11
Glycerol-methanol	35.08	58.97
Glycerol-hexadecane	42.80	50.44

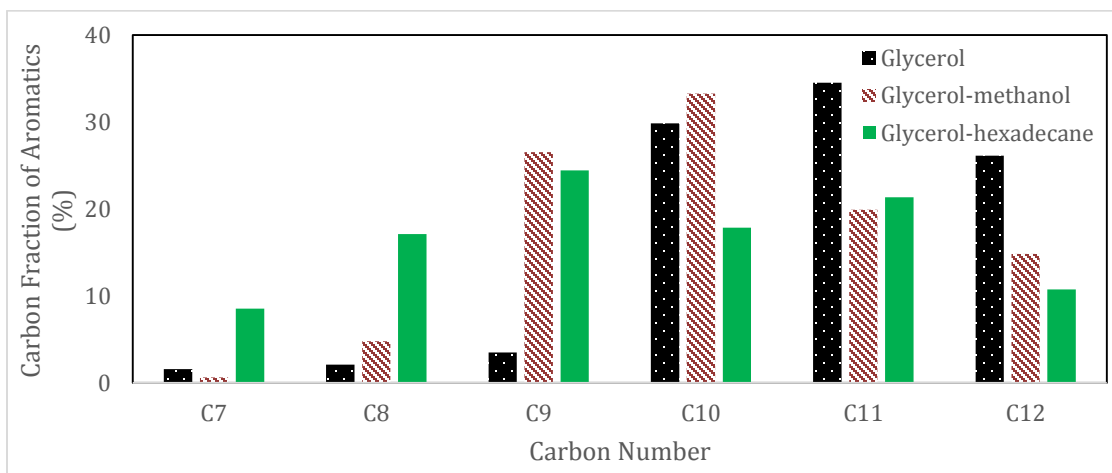


Figure 4- 11 Aromatic compounds distribution before and after co-feeding over alumina at 470°C

The added reactive intermediates through cracking of long-chain paraffin would potentially have the similar impact as alcohols on the enhancement of constructive condensation reactions. Dealkylation step could also occur more favorably due to the presence of more proton-donors in the glycerol-long chain paraffin runs. Moreover, glycerol intermediates would likely have more opportunities to reach other reactive intermediates and undergo Lewis-acid favored mechanisms to directly form lighter aromatics such as xylenes. Between the selected alkanes, normal-hexadecane had higher performance efficiency in terms of suppressing the coke formation and increasing the gasoline-range aromatic compounds, which might be due to the slightly higher cracking conversion of it than dodecane.

Fig. 4-9, Table 4-6, and Fig. 4-10 compare the results from individual catalytic conversion of glycerol, co-processing glycerol and methanol (as the preferred alcohol), and co-processing glycerol and n-C₁₆ (as the preferred long-chain paraffin). Even though hexadecane comparing to glycerol and methanol had significantly lower conversion in the process, it interestingly increases the selectivity to aromatics and mitigates the formation of carbon deposit on the catalyst. Moreover in the run of glycerol-hexadecane, aromatic compounds distribution noticeably shifts from the larger undesired range to the lighter one. Chapter 5 will elaborate the influence of co-feeding hexadecane on glycerol catalytic conversion in more details.

Chapter 5- Co-Conversion of Glycerol and n-C₁₆ to Gasoline-Range Aromatics over Alumina

5.1 Scope of Work

In this chapter, a detailed study to determine the influence of glycerol-hexadecane composition ratio on the products through catalytic conversion over alumina at 470°C was performed. Consequently, it was proposed how co-cracking of n-C₁₆ might directly impact the catalytic conversion of glycerol over alumina. Later on, a brief study was completed to discuss the potential effect of the operational temperature on co-processing 50/50 wt.% glycerol/hexadecane.

5.2 Individual Catalytic Cracking of Normal Hexadecane

To track the impact of co-cracking hexadecane on glycerol and its products, catalytic cracking of pure hexadecane was run under the same operational condition as described in Chapter 4, at first. On the contrary to the conversion of glycerol, the cracking conversion of hexadecane was relatively low (18.5%). This low conversion might be due to the absence of Bronsted acid sites on the catalyst to trigger the propagation step, as it was discussed earlier in section 4-3. Moreover, the selected operational temperature would not significantly boost the thermal activity of hexadecane, as commonly thermal cracking processes of alkanes are operated in temperatures higher than 700°C.

Fig. 5-1 (a) accounts the phase yield distribution of the product streams (unconverted hexadecane in the liquid phase is subtracted). Both produced gas phase and

carbon deposit constituted less than 7 wt.% yields, which could be attributed to low activity of hexadecane on the catalyst. Alkane products had the highest selectivity among the formed components (Fig. 5-1 (b)). In contrast, the amount of produced aromatics was very low. 3.5% selectivity to aromatics indicates that hexadecane by itself is not prone to proceed in cyclization reactions over alumina. Selectivity to olefins (light olefins, butylene, and condensed olefins) was relatively high, and some were detected in the range of C₅ and C₇ aside non-condensable olefins (Fig 2.c). 9% selectivity to hydrogen could also confirm that cracking of hexadecane over alumina would likely provide noticeable protons in the process as intermediates.

Low conversion would evidence that alumina acid sites (Lewis acid) in conjugation with selected operational parameters are not efficient enough for paraffin to crack. However, olefins and proton (H⁺) are often considered as intermediate products in the paraffin cracking, and they mostly undergo further reactions to convert to more stable compounds, such as alkanes and aromatics [60]. By co-cracking hexadecane next to glycerol, the overall reaction mechanism may change. Before completing the saturation process of the produced olefins and proton intermediates to lighter alkanes and hydrogen molecules, they may be consumed in different reactions and interact with glycerol and its intermediates to convert to new products.

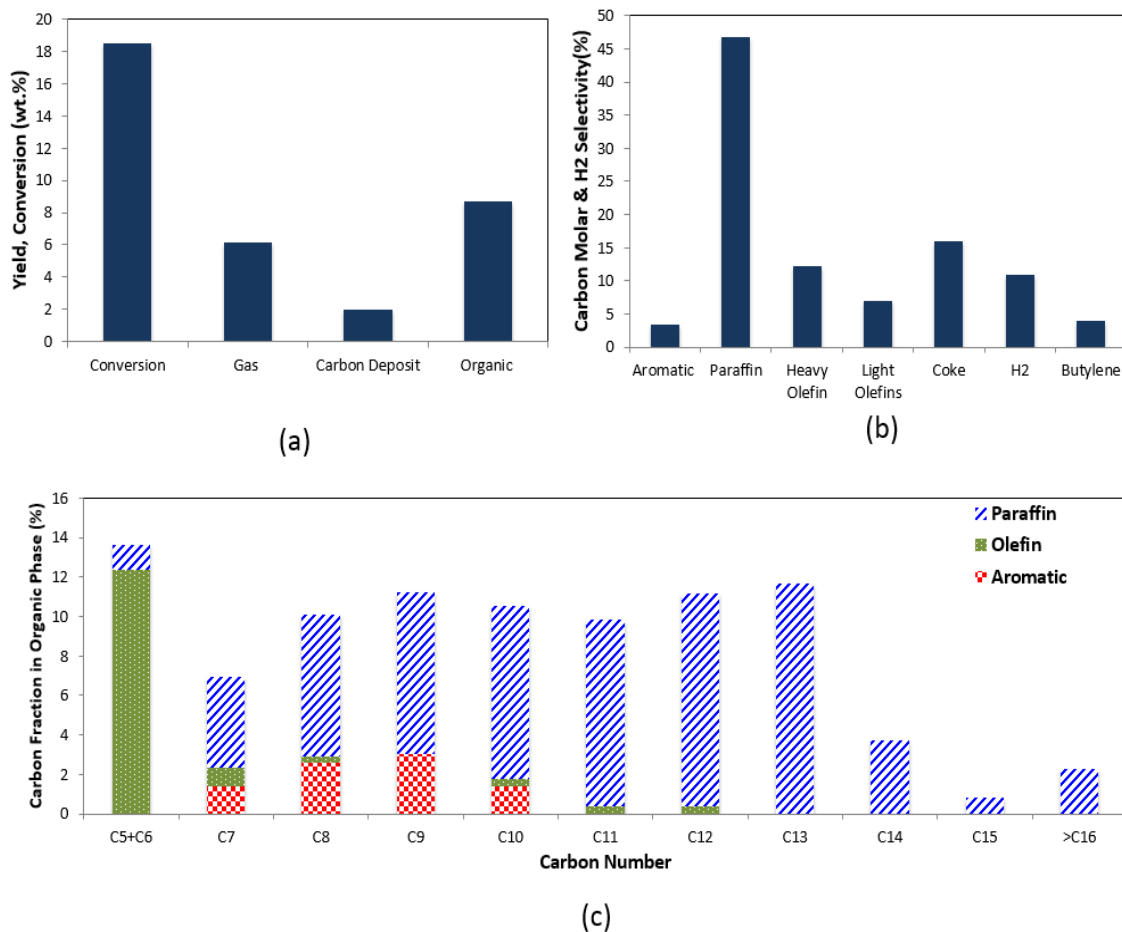


Figure 5- 1 Catalytic cracking of hexadecane over alumina at 470°C, phase yield (a), major products selectivity (b), and carbon fraction of organic phase (c)

5.3 Co-Processing Glycerol and Normal Hexadecane with Different Composition Ratios

Although it was mentioned in chapter 4 to maintain glycerol as the major feed and n-C₁₆ as minor, here hexadecane was co-fed with 3 different ratios in order to compare the final products and potential intermediates through the process. Varying the glycerol/hexadecane ratio might facilitate to track the impact of co-processing on the glycerol catalytic conversion mechanism in more details.

5.3.1 Effect of Co-Feeding on Conversion

Different glycerol/hexadecane concentrations of 0/100, 25/75, 50/50, 75/25, and 100/0 wt.% were fed to the reactor. Glycerol to hexadecane molar ratio were 1.221, 0.407, and 0.136 respectively for the co-fed experiments. To make comparative analyses, all of the experiments were run under identical conditions. The presence of glycerol had a negative impact on the catalytic cracking conversion of n-C16. Fig. 5-2 shows that the conversion of C16 was 18.49% while there was no added glycerol, and this parameter dropped to 9.86% while glycerol/hexadecane ratio was 75/25 wt.%.

High tendency of glycerol to form carbonaceous deposit on the catalyst surface would be the major reason to restrict the further cracking of hexadecane. The presence of carbon deposit and some oxygenated compounds such as water on the catalyst through glycerol cracking would block the acid sites and diminish the total acidity. In consequence, hexadecane has less chance to access to the acid sites to convert.

On the other hand, conversion of glycerol was about 100% for all of the runs since the presence of Lewis acid sites and high operational temperature favor the initial dehydration reaction [61].

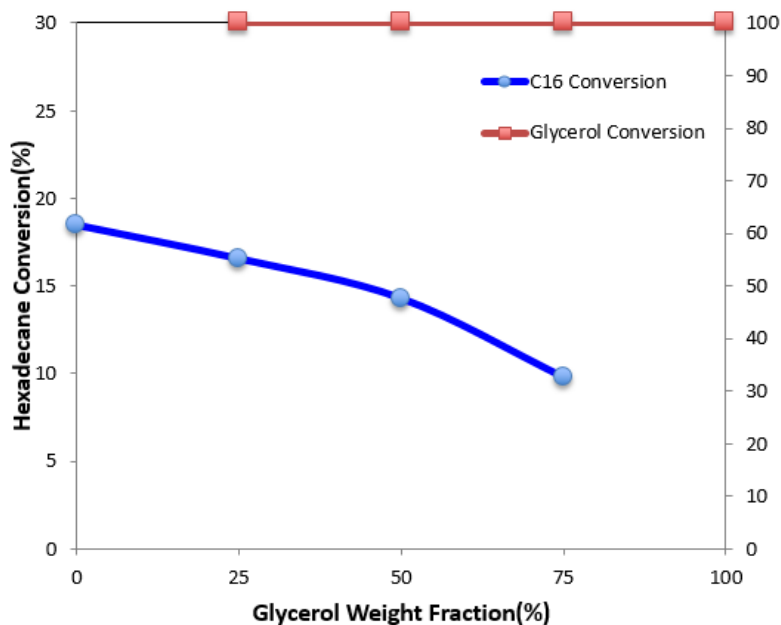


Figure 5- 2 Influence of co-feeding glycerol and hexadecane on conversion

5.3.2 Aromatization of glycerol in the presence of hexadecane

The influence of co-feeding ratio of glycerol and hexadecane on the distribution of final products was also studied. The detailed results are shown in Fig. 5-3 and Fig. 5-4. The impact of co-feeding on producing organic compounds becomes clearer by tracking the evolution of organic phase yield in Fig. 5-3 (a). The co-feeding of 25 wt.% hexadecane had the highest organic phase yield (13.61 wt.%). However, in all co-fed cases, the quantity of products in the organic phase was higher than cases which glycerol or hexadecane was fed individually. Aqueous phase and carbon deposit yield continuously fell by increasing the hexadecane weight fraction. The aqueous phase yield dropped by around 50% while 25 wt.% C₁₆ was introduced to the process. Decrease in the aqueous phase and solidified products would occur because of two implemented modification in the process:

1. Concentration of glycerol as the major factor for excessive dehydration and coke formation is decreasing in the process.
2. Introducing hexadecane is effectively rerouting the glycerol common reaction pathways.

To eliminate the impact of glycerol concentration and evaluate the effect of co-feeding hexadecane more precisely, Fig. 5-4 details the yield and selectivity of the products “per unit of converted glycerol” (\bar{Y}_i and \bar{S}_i). Fig. 5-4 (a) confirms that after introducing hexadecane, the aqueous phase yield per gram of glycerol drastically decreased; whereas, $\bar{Y}_{organic\ phase}$ significantly increased.

Co-feeding hexadecane had a direct effect on the selectivity to aromatics as well. Fig. 5-3 (b) indicates that even the glycerol-diluted run under 75/25 hexadecane to glycerol wt.% ratio had higher selectivity to aromatics than while feeding the pure glycerol. Feeding 25 wt.% hexadecane with 75 wt.% glycerol yielded to the highest carbon molar selectivity to aromatics (41%). However it is noted that under this condition, carbon deposit selectivity was still higher than the desired product’s selectivity.

Comparatively, co-feeding hexadecane and glycerol with 75/25 wt.% ratio produced more aromatics than carbonaceous deposit on the catalyst, and the organic phase had the highest phase yield among the distributed phases. $\bar{S}_{aromatics}$ continuously increases by introducing more hexadecane to the process. Fig. 5-4 (b) clearly shows the synergetic effect of hexadecane and glycerol to produce aromatics.

On the other hand, the amount of formed carbon deposit per mole of glycerol dropped significantly by introducing hexadecane to the process, but slightly started rising by increasing the hexadecane/glycerol ratio.

Fig. 5-3 (c) and Fig. 5-4 (c) summarize the evolution of gaseous streams while co-feeding hexadecane and glycerol. Following the trend of olefins and hydrogen production might be a key factor to confirm the positive influence of hexadecane. Selectivity to light olefins and C₄ fraction dropped in the co-fed runs comparing to the individual catalytic conversion of hexadecane and glycerol. Moreover, the evolution of H₂ selectivity in Fig. 5-3 (c) shows that there is a big gap of hydrogen selectivity between individual cracking of hexadecane and cracking hexadecane next to 25 wt.% glycerol. In other words, the presence of glycerol in the process adversely affected the production of hydrogen gas.

Fig. 5-4 (c) also represents that \bar{S}_{CO} and \bar{S}_{CO_2} generally increased by introducing more hexadecane. This trend would be a notable evidence of the influence, as the dilution of glycerol in the process was increasing the selectivity of CO and CO₂.

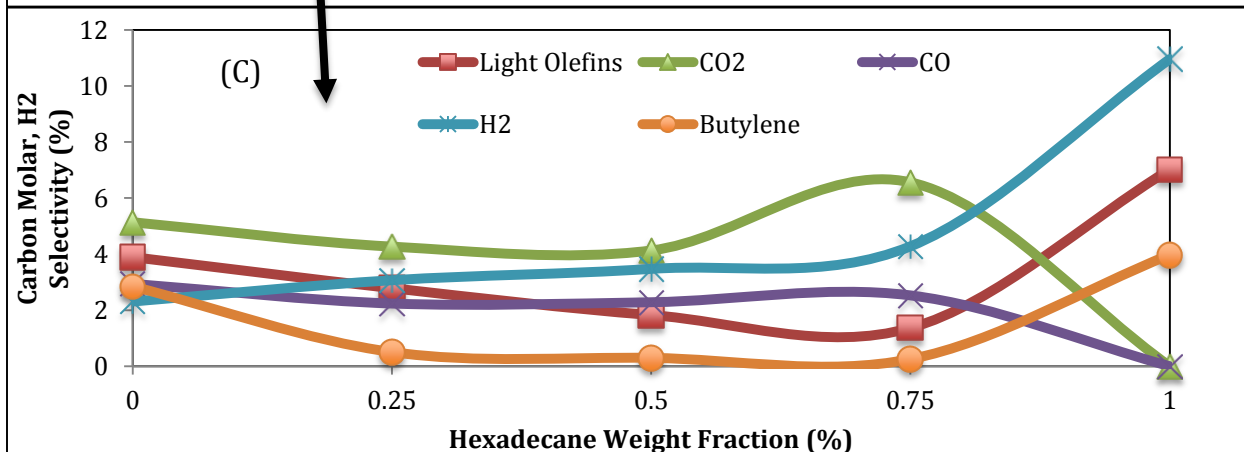
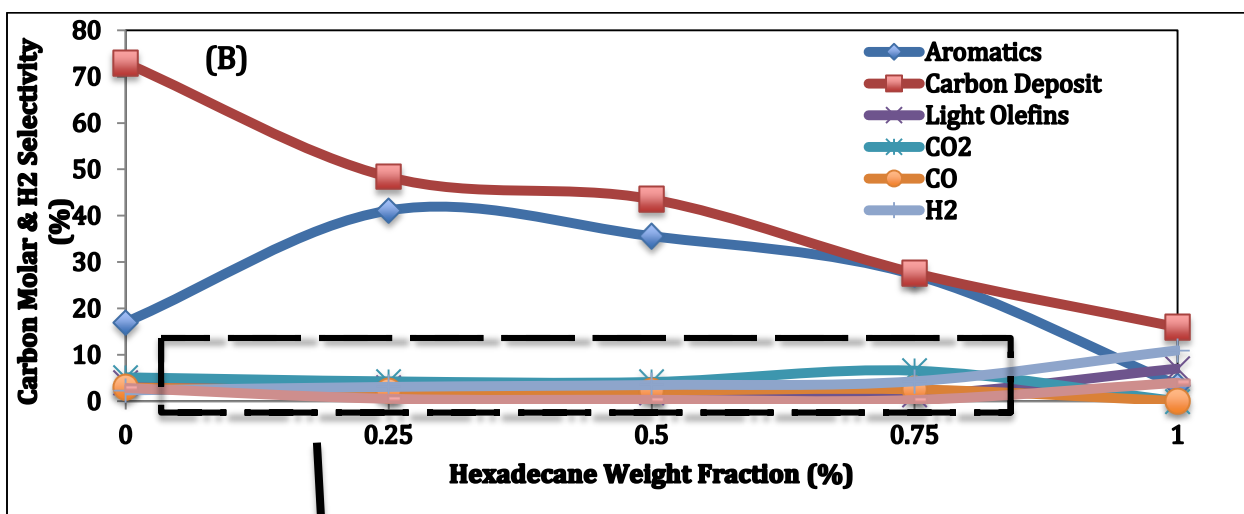
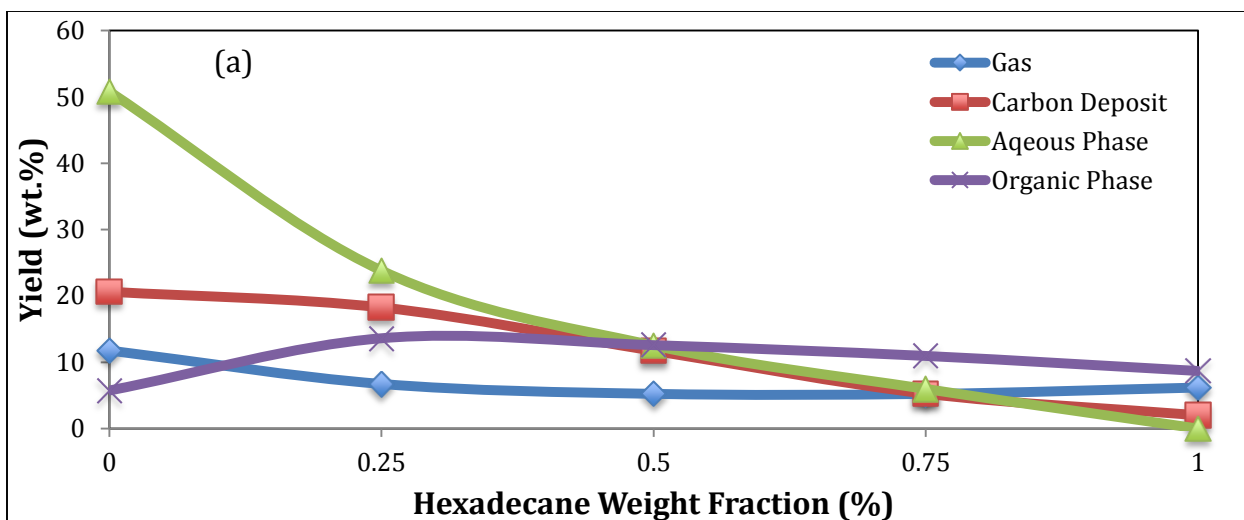


Figure 5- 3 Influence of co-feeding hexadecane and glycerol on product distribution, phase yield (a), products selectivity (b), and gaseous products selectivity (c).

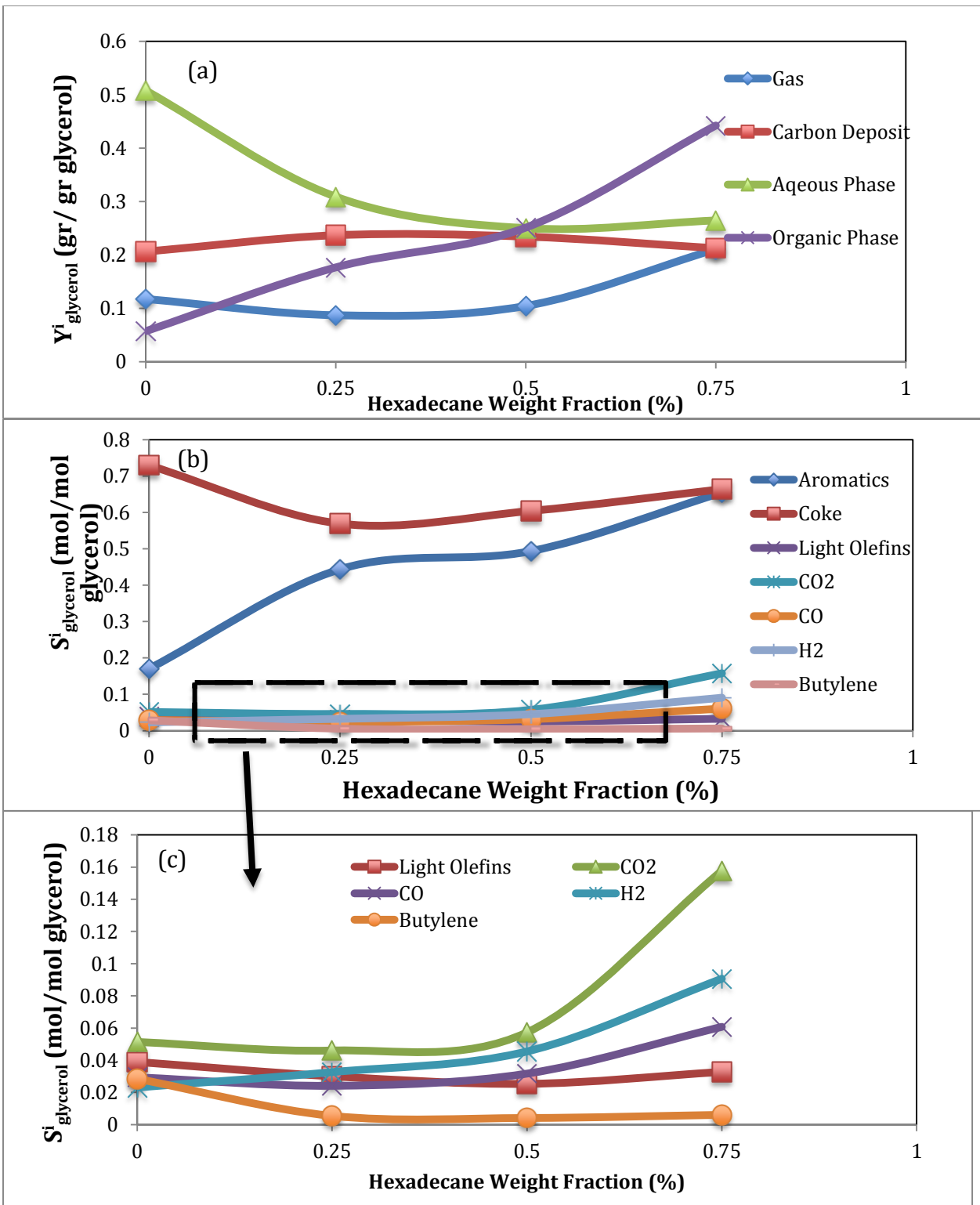


Figure 5- 4 Influence of co-feeding hexadecane on product distribution, phase \bar{Y}_i (a), products \bar{S}_{i1} (b), and gaseous products \bar{S}_i (c)

5.3.3 Oxygen Distribution among Formed Products

Although details for oxygenated components are not fully provided, Table 5-2 indicates a comparison among different co-fed runs for oxygen distribution among three aqueous, gas, and organic phases after catalytic conversion in the process, based on elemental analyses. Introducing hexadecane to the process significantly decreased the amount of oxygen concentrated in the aqueous phase.

On the other hand, a considerable fraction of initial moles of oxygen appeared in the organic phase after co-feeding hexadecane. At 50/50 hexadecane to glycerol wt.% ratio, 24% of the initial oxygen migrated to the organic phase, whereas through the individual glycerol cracking only 2.64% of the initial oxygen was found in the organic phase, and almost 76% of the oxygen in the feed was removed by dehydration. This evolution may show the effect of co-processing hexadecane on the path of glycerol to the products. The removed oxygen through the gas stream was also influenced by hexadecane weight fraction. As a general trend, the amount of oxygen removed through decarbonylation and decarboxylation reactions grows by increasing hexadecane/glycerol ratio in the process.

Although high concentration of oxygen in the organic phase would not be very suitable, the drop in the excessive dehydration reaction is a desired change. In the presence of hexadecane, oxygenated compound would likely desorb from the catalyst and migrate to the liquid organic phase, which has a higher heating-value, before undergoing severe carbonization and dehydration reactions.

Table 5- 1 Oxygen distribution among different phases through hexadecane and glycerol co-feeding runs

Hexadecane/Glycerol Ratio	0 mole in aqueous phase	0 mole in gas phase	0 mole in organic phase
	<i>0 mole in feed</i> (%)	<i>0 mole in feed</i> (%)	<i>0 mole in feed</i> (%)
0/100	75.88	9.27	2.64
25/75	46.18	8.15	15.54
50/50	37.38	10.26	23.89
75/25	25.54	21.48	35.25

5.3.4 Influence of n-C₁₆ on Glycerol Catalytic Conversion Mechanism over Alumina

Co-feeding hexadecane noticeably influences the glycerol catalytic conversion reaction pathways over alumina. Increasing the H/C_{eff} ratio in the process due to the presence of hexadecane would be effective for this influence. Although catalytic cracking conversion of hexadecane is low, it rises with increasing the n-C₁₆/glycerol ratio. Co-processing 75/25 wt.% hexadecane/glycerol most likely has the highest H/C_{eff} ratio among the co-fed runs. With increasing H/C_{eff} ratio, aromatic and olefin yield increase in the process, and coke yield decreases [31].

In contrast to the individual catalytic conversion of glycerol, the introduction of hexadecane to the process results in more hydrocarbon intermediates, which provides more opportunities to glycerol intermediates to interact with the hydrocarbon intermediates. As discussed earlier, in the co-processing runs comparing to cracking the hexadecane individually, selectivity to light olefins (ethylene and propylene) and C₄ fraction olefins significantly decreased. Moreover, selectivity to hydrogen also noticeably dropped as soon as glycerol was introduced. This trend accounts that olefins and H⁺ may be consumed in some other reactions, resulting in higher cyclic organic compounds in the liquid phase.

Diels-Alder reaction is a Lewis-acid-favored mechanism likely may occur over alumina in the process to form rings. It is a reaction between a conjugated diene and a dienophile (an alkene) to form a cyclohexene. Diels-Alder mechanism is readily facilitated by electron withdrawing groups on the dienophile and electron donating groups on the diene [62]. Even though Diels-Alder mechanism is more intended to occur over very strong Lewis acid sites at lower temperatures, it is also possible that the reaction proceeds in the lower acidity but higher temperatures to activate the catalyst [63]. A produced diene olefin through hexadecane cracking (such as butadiene) might react with non-tautomerized 1, 2-dihydroxypropene as a dienophile over Lewis acid and form an oxygenated cyclic hydrocarbon. Later on, this compound may undergo further dehydration over the catalyst and create an alkylated aromatic such as toluene.

Another cyclic mechanism that may favorably occur over Lewis catalyst and high temperatures is Ene reaction, which is a reaction between an alkene with allylic hydrogen (ene) and an enophile to produce a pericyclic compound [64]. So, the carbonyl group of hydroxyacetone (enophile) might possibly undergo a carbonyl-ene reaction with allyl-contained olefins (ene) such as propylene and create a new pericyclic intermediate. In the case of carbonyl-ene reactions, Lewis acid activation and elevated temperatures are often required [65]. The produced intermediate may further dehydrate over Lewis acid site (the same mechanism as the first dehydration step of glycerol over Lewis acid) and turn into a conjugated diene component. Therefore, the produced diene and an olefin such as ethylene may undergo another Diels-Alder reaction mechanism and generate a cyclic compound. Converting the cyclic compound to an aromatic product such as xylene might occur via removing methanol group and hydrogen transfer reactions.

The presence of hydrocarbon intermediates from the co-cracking of hexadecane may also increase the chance of hydroxyacetone and glycerol to reach other proton-donor sources over the catalyst and prevent from excessive self-oligomerization and dehydration. Therefore, the oligomerized products have higher H/C effective ratio and less number of heteroatoms in the structure than the self-oligomerized compounds (in the absence of hydrocarbon intermediates, glycerol intermediates would reach each other and increase the number of oxygen in the structure, resulting in unsaturated intermediates.). Moreover, the produced H^+ from $n-C_{16}$ would also directly attack the glycerol intermediates and facilitate the deoxygenation reactions.

Consequently, the formed compounds resulted from the interaction of hydrocarbon and glycerol intermediates may more easily desorb from the catalyst surface and migrate to the organic phase rather than forming excessive carbon deposit on the catalyst surface. This could explain why co-processing hexadecane increases both the yield and oxygen concentration of liquid organic phase in the products.

The influence of co-cracking on the reaction pathway of glycerol catalytic conversion would be more complex as hydrocarbon intermediates could also have impact on large produced aromatics via reactions such as dealkylation and deprotonization (section 4-3-4). Here it is mostly focused on the potential direct effects of co-produced olefins and protons on the glycerol intermediates to form lighter aromatics over Lewis acid catalyst. Fig. 5-5 summarizes the potential direct influence of co-processing hexadecane on the reaction pathway for glycerol catalytic conversion over alumina at 470°C.

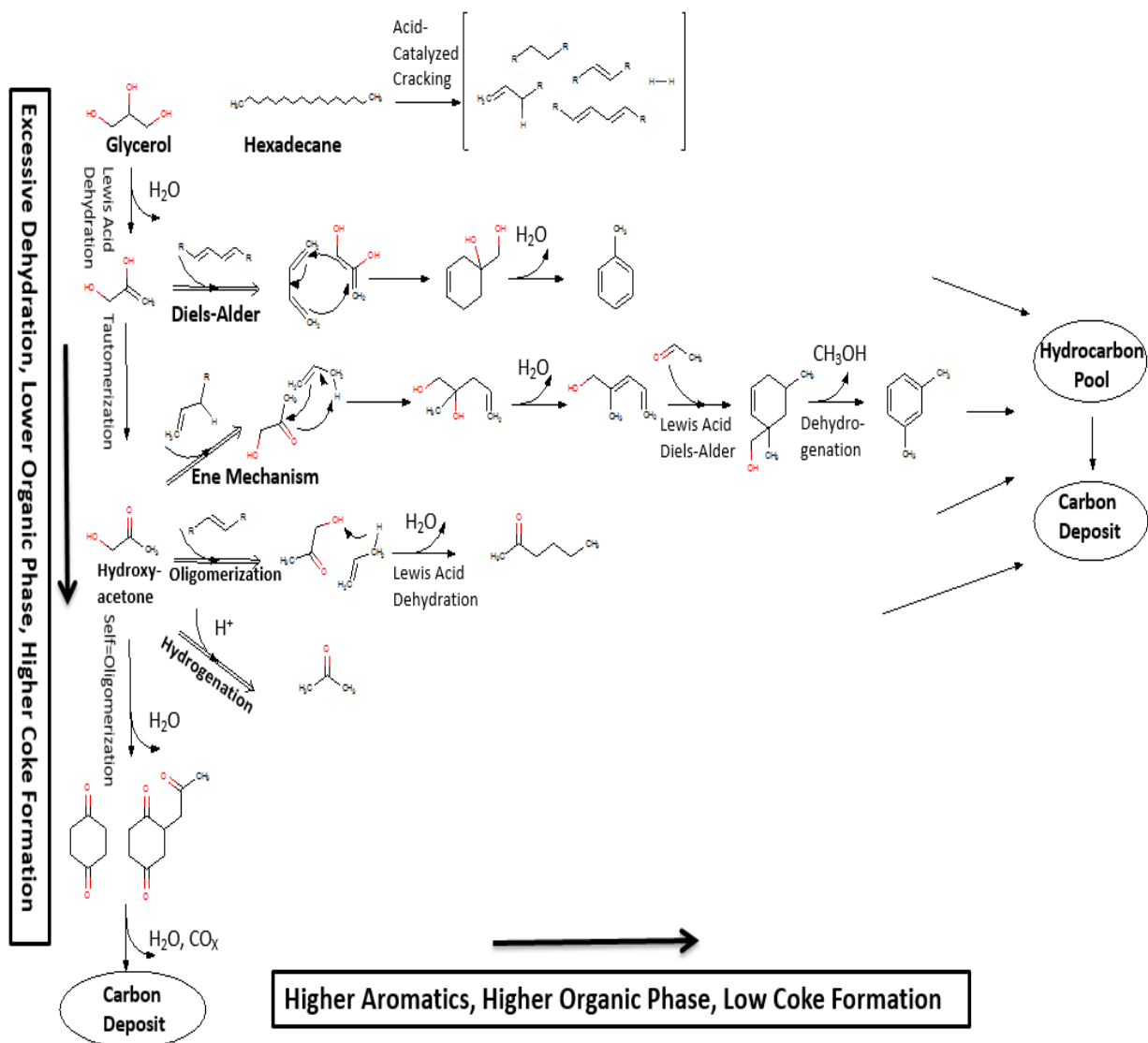


Figure 5- 5 proposed reaction pathway for glycerol catalytic conversion over alumina at 470°C, after introducing hexadecane.

5.3.5 Effect of Glycerol-Hexadecane Ratio on Aromatic Compounds Distribution

The evolution of aromatics distribution before and after introducing hexadecane to glycerol is also noticeable. Fig. 5-6 clearly shows a shift in the range of produced aromatics after co-feeding hexadecane. While glycerol was fed individually, the majority of formed

aromatics were in the range of heavy molecules (C10-C12); but the formation of toluene, xylenes, and trimethylbenzenes (TMBs) were insignificant. Moreover, the presence of heavy aromatics such as Phenanthrene, 3,6-dimethyl- (C16H14) in the coke soluble stream also confirms that glycerol is more inclined to form large aromatics than desirable gasoline-range ones over alumina. Introducing hexadecane to the process next to glycerol shifted the distribution of produced aromatics to a lighter range (C7-C9), and selectivity to large aromatics such as C12 aromatics significantly suppressed. Additionally, the formation of polyaromatics such as Phenanthrene, 3, 6-dimethyl- in the 50/50 wt.% hexadecane/glycerol coke soluble stream was not in the detectable range.

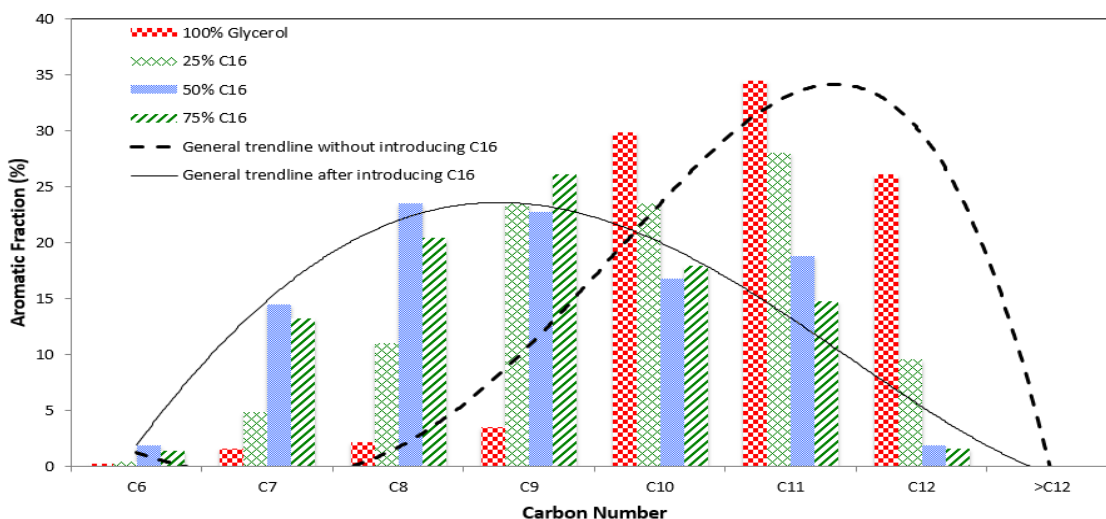


Figure 5- 6 Carbon molar fraction of aromatics for different hexadecane/glycerol ratios

By introducing 25 wt.% hexadecane, although the concentration of C10 and C11 aromatics were still high, selectivity to toluene, xylenes, and TMBs considerably rose. In the all of co-fed runs, regardless of the diversity and the fraction of formed aromatics ranges, O-xylene had the highest concentration among all aromatics, and C12 aromatics had the least one. The tendency to formation of smaller aromatics after introducing

hexadecane might be due to the influence of hexadecane intermediates on glycerol catalytic cracking mechanism, which was discussed earlier. As Al_2O_3 has a high activity to glycerol conversion, and due to the hydrogen deficient structure of glycerol (high oxygen content), excessive oligomerization and condensation is the proceeding mechanism that leads to mainly form large cyclic molecules [66]. Majority of these formed compounds solidify as coke on the catalyst surface and the small amount of them liquefy in the large aromatics range.

By introducing new reactive intermediates to the process through hexadecane, glycerol intermediates could undergo different reaction pathways such as diels-alder reactions to form smaller aromatics and stabilize more quickly and desorb from the catalyst surface. Increasing $\text{H}/\text{C}_{\text{eff}}$ ratio significantly decreases the catalyst deactivation rate [67]. So, suppressing the excessive coke formation and the formation of products with higher $\text{H}/\text{C}_{\text{eff}}$ ratio in consequence of possible reactions between hexadecane and glycerol intermediates such as Diels alder, Ene, and oligomerization would account that a significant portion of produced aromatics desorb from the catalyst surface before leading to form large molecules.

The figure also indicates that introducing hexadecane does not affect the benzene production. This trend indicates that the formation of benzene is not favorable as compared with that of toluene, xylenes, or TMBs. The least selectivity to benzene might be due to the fact that the direct formation of six-membered rings requires highly unstable reactive complexes; whereas, the formation of toluene, C8, or C9 aromatics is not like that[68].

5.4 Effect of Temperature on Co-Catalytic Conversion of Glycerol and Hexadecane

To evaluate the influence of temperature on co-processing glycerol and hexadecane another set of experiments were run under the identical and hexadecane/glycerol ratio of 50/50 wt.%, while the studied temperatures were 400, 470, 540, and 610 °C. Fig. 5-7 and 5-8 represent the effect of temperature on product streams in more details. As it can be expected, the cracking conversion of hexadecane continuously rose by increasing the temperature, while the conversion of glycerol was almost complete in all of the runs (Fig. 5-7).

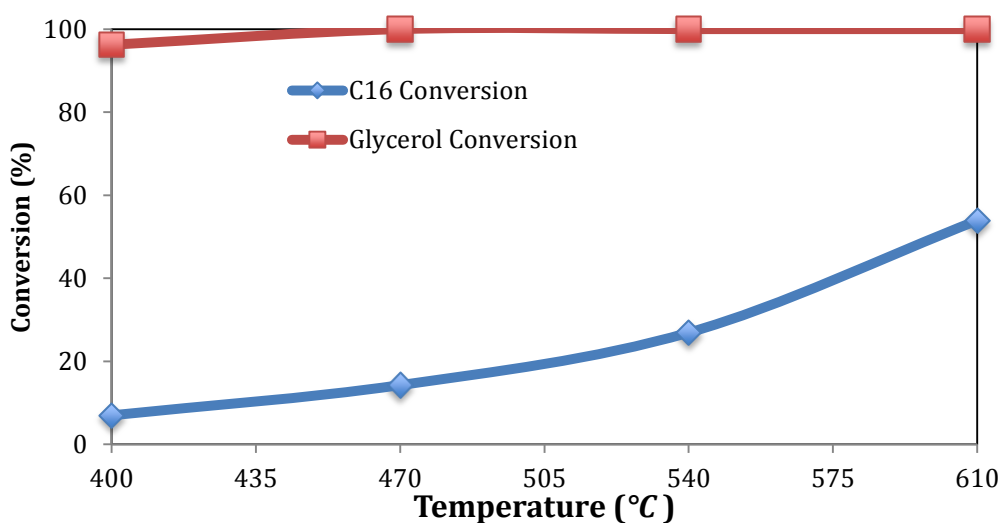


Figure 5- 7 Influence of temperature on catalytic cracking conversion of hexadecane and glycerol over alumina

As of following the trends in Fig. 5-8 (a), by increasing the temperature, yield to gaseous products kept rising gradually, and yield to carbon deposit did not fluctuate substantially. At 400°C, aqueous phase yield was relatively high, and organic phase yield was low. By increasing the temperature organic phase turned to the major phase and the

yield to the aqueous phase dropped. However, in higher temperatures, the amount of aqueous and organic phase did not change significantly, and the gaseous stream turned to the most considerable phase.

The co-catalytic process run at 470°C had the highest selectivity to aromatics, whilst in higher temperatures aromatics selectivity decreased gradually. On the other hand, hydrogen and olefins selectivity at 470°C were lower than at 400°C, 540°C and 610°C. Carbon molar selectivity to coke substantially decreased by increasing temperature as well, but carbon dioxide and carbon monoxide selectivity did not change noticeably (Fig. 5-8 (b)).

Fig. 5-8 (c) details the distribution of aromatic compounds in 50/50 wt.% hexadecane/glycerol ratio at different temperatures. Running the process at 540°C had the highest toluene and xylenes fraction among the produced aromatic compounds, and co-processing at 400°C led to form the highest C₁₁ aromatic fraction. However by comparing the influence of different co-processing ratios at the same temperature (Fig. 5-6) and different temperature at the same ratio (Fig. 5-8 (c)) on the aromatic compounds distribution, it seems varying the hexadecane/glycerol ratio has higher impact on the fractions than altering the operational temperature within 200°C range.

Following the trending for aromatics and coke selectivity under the different temperatures, it seems that co-feeding process is limited by the temperature because of two reasons:

- 1- The reactivity of alkanes dramatically drops by decreasing the operational temperature [69]. In consequence of low cracking conversion of hexadecane over Al₂O₃ at 400°C, the amount of formed intermediates such as olefins and protons is not adequate to

affect the reaction pathways of glycerol catalytic conversion. Therefore, the general production trending for the run with 50/50 glycerol to hexadecane wt.% at 400°C is comparatively similar to that of individual glycerol catalytic conversion; high aqueous phase yield, high coke selectivity, and low aromaticity.

2- Cyclic-favored reactions over Lewis acid catalysts such as Diels-alder reaction are reversible in high temperature (retro reactions) [63]. So in higher temperatures like 610°C, either the desirable reactions to form aromatics such as Diels-Alder, Ene, and condensation do not proceed, or the formed cyclic compounds are unstable and undergo open-ring reactions. As a result, even though the cracking conversion of co-fed hexadecane is significantly high, the product stream is poor in aromaticity and high in selectivity to gaseous olefins.

Considering the temperature limitations for co-feeding hexadecane and glycerol, there might be an intermediate temperature to optimize the production of gasoline-range aromatics, which among the studied temperatures, the highest selectivity to aromatics and organic phase yield occurred at 470°C.

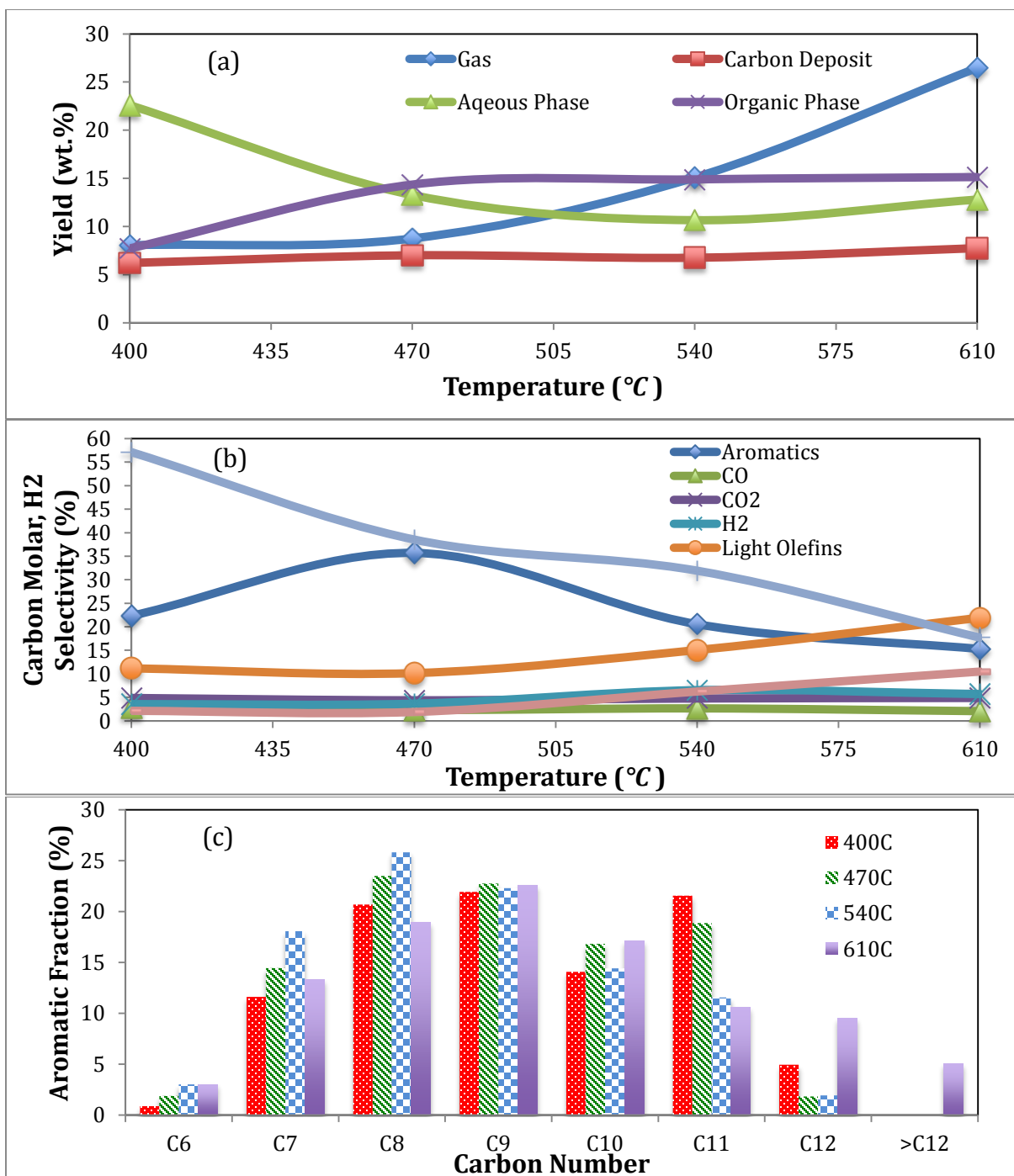


Figure 5- 8 Effect of temperature on (a) phase yield, (b) selectivity, and (c) aromatics distribution while co-catalytic cracking of 50/50 wt.% hexadecane and glycerol over alumina

5.5 Conclusion

The reaction pathway of catalytic conversion of glycerol over Al_2O_3 with and without introducing long-chain paraffin compound model (hexadecane) has been proposed. Glycerol over alumina catalyst is very reactive and due to the self-oligomerization reactions of its intermediates in the absence of proton-donor reactants led to around 73% coke carbon molar selectivity and excessive dehydration. Moreover, selectivity to aromatics was very insignificant and most of it was in the large undesired range.

By introducing hexadecane to the process, the intermediates of glycerol have more opportunities to react with reactive components including olefins and protons under favored mechanisms such as Diels-Alder and Ene reactions to create more desired products. Co-feeding 25 wt.% hexadecane next to glycerol significantly increased the aromatics selectivity and suppressed the coke and aqueous phase formation. Additionally, after introducing hexadecane, the distribution of aromatics noticeably shifted to the gasoline-range area and the fraction of heavy aromatics such as C_{12} aromatics dropped, which accounts by increasing $\text{H}/\text{C}_{\text{eff}}$ ratio in the process the products desorb from the catalyst surface at more ease.

Studying the influence of temperature on co-feeding process indicates that temperature is a limiting factor for the purpose of aromatics formation. Due to the low cracking conversion of hexadecane in lower temperatures, the results from co-feeding was more like the trending for the individual catalytic conversion of glycerol. On the other hand, high operational temperatures would favor the reversed reactions of aromatic formation such as retro-Diels-Alder or retro-Ene mechanisms resulting in less aromatics

selectivity and high gas phase yield. In the studied temperatures, the highest selectivity to aromatics and the least undesired products occurred at 470°C.

Chapter 6- Conclusion

6.1 Conclusion

Nowadays, glycerol as the main by-product of biodiesel production has gained more attention to utilize and convert to value-added chemicals. It was evaluated that due to the impurity of the generated crude glycerol in the biodiesel production plant, it is difficult and costly to purify and apply it in sensitive areas such as food industry or personal care. Hence, efforts have been made to find ways to convert glycerol to valuable industrial feedstocks via less costly processes. Catalytic conversion of glycerol to produce green products and olefins has been found to be one of the effective processes to utilize cheap and abundant glycerol.

Unlike the previous catalytic conversion of glycerol studies that were mostly performed over Bronsted acid-rich zeolite catalysts, here in this work catalytic conversion of glycerol was evaluated over less-expensive Lewis-acid alumina catalyst. Glycerol over alumina catalyst at 470°C was very reactive and due to the self-oligomerization reactions of its intermediates, in the absence of proton-donor reactants and strong Bronsted acid sites, the conversion led to around 73% coke carbon molar selectivity and excessive dehydration. Moreover, selectivity to aromatics was very insignificant and most of it was in the large undesired range.

To limit the excessive formation of carbon deposit on the catalyst and enhance the production of liquid aromatics, methanol and ethanol as compound models of alcohols, and dodecane and normal hexadecane as compound models of long-chain paraffin were co-fed next to glycerol with 25/75 wt.% ratio. Introducing alcohols to the process significantly

increased the selectivity to aromatic compounds by 17.7% and suppressed the formation of carbon deposit on the catalyst surface by 14.1%. However, the major drawback of co-feeding alcohols could be the relatively low selectivity to valuable gasoline-range aromatics such as toluene and xylenes.

Introducing long-chain paraffin next to glycerol over alumina under the same operational conditions enhanced the formation of gasoline-range aromatics, in addition to the net promotion in the total liquid aromatic production and decrease in the coke formation. Even though n-C₁₆ had noticeably low cracking conversion on alumina catalyst at 470°C, co-processing 25 wt.% n-C₁₆ next to 75 wt.% glycerol had the highest selectivity to gasoline-range aromatics and the lowest production of undesired stream including aqueous phase compounds and carbon deposit.

As it was found that co-feeding hexadecane would have the best performance among the selected compound models, the influence of hexadecane on the catalytic conversion of glycerol at 470°C was studied in more details with different hexadecane-glycerol composition ratios, and the reaction pathway of catalytic conversion of glycerol over Al₂O₃ with and without hexadecane was proposed and compared. By introducing hexadecane to the process, the intermediates of glycerol would have more opportunities to react with reactive components including olefins and protons and undergo desired mechanisms such as Diels-Alder and Ene reactions to create more favorite products. Additionally, after introducing hexadecane, the distribution of aromatics noticeably shifted to the gasoline-range area and the fraction of heavy aromatics such as C₁₂ aromatics drops. This accounts that by increasing protons and olefins in the process the products would

desorb from the catalyst surface at more ease and dealkylation mechanisms would proceed further.

Studying the influence of temperature on co-feeding process accounted that temperature would be a limiting factor for the purpose of aromatics formation. Due to the low cracking conversion of hexadecane in lower temperatures, and the potential reversed reactions of aromatic formation in high operational temperatures, there might be an optimum temperature in order to utilize the co-feeding process in terms of gasoline-range aromatics production. In the studied temperatures, the highest selectivity to aromatics and the least undesired products occurred at 470°C.

6.2 Recommendation for Future Work

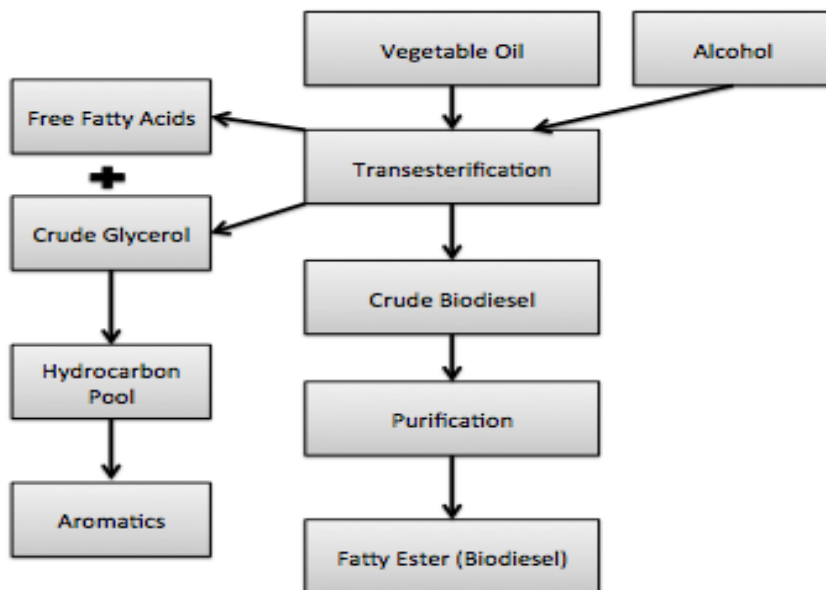


Figure 6- 1 Simplified recommended process for co-processing free fatty acids and crude glycerol in a transesterification process

Evaluating the co-processing of glycerol and fatty acids over a Lewis-acid catalyst like alumina would shed some light on the feasibility of the proposal for the once-through converting of crude glycerol to valuable industrial feedstocks such as aromatics in a biodiesel production process (Fig. 6-1). As it was discussed in 1.3.1, free fatty acids are also another by-product of biodiesel production through transesterification process that commonly contain long-chain hydrocarbon (saturated or unsaturated) in their structure. An effective co-processing setup between glycerol and free fatty acids can create a beneficial in-situ solution in order to convert the by-product of biodiesel production process to value-added chemicals.

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- 3.