TECHNO-ECONOMIC ANALYSIS OF ALTERNATIVE PATHWAYS FOR ISOPROPANOL PRODUCTION

A Thesis

by

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ABSTRACT

The price fluctuations and unpredictability of a secure supply of fossil fuels create uncertainty in chemical production. One of the chemicals impacted by uncertainty is isopropanol, which has traditionally been manufactured from propylene. The shale gas boom has led to propylene shortages. Along with the high growth rate of propylene based-products, the propylene market has been tight and prices are expected to increase. Therefore, it is necessary to identify alternative, cost-effective, and sustainable pathways for the production of isopropanol. Isopropanol is projected to grow annually at a rate of about two percent across the globe. It is primarily used as a solvent in cosmetics, in personal care products, and in pharmaceutical products. Other uses include as a motor oil in the automotive industry, and as a cleaning and drying agent in the electronics industry. The objective of this research is to find alternative pathways to produce isopropanol and to select viable pathways while considering technology and economic factors. The methodology to achieve this objective includes branching and matching, prescreening, pathway selection, techno-economic analysis, and selecting the most sustainable pathway. A superstructure is created to show routes that can produce isopropanol from a variety of feedstocks. The techno-economic assessments of processes are also performed to compare the profitability of possible processes. The result shows that the propane dehydrogenation is still the best pathway to produce propylene. The result also reveals that the most promising pathway for isopropanol production is direct hydration. The advantages of the direct hydration method over the indirect hydration method include less dependency of

annual ROI on the price of propylene (the feedstock of hydration processes), and avoidance of corrosion and environmental problems.

DEDICATION

To my parents

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1. INTRODUCTION

1.1 Overview

Crude oil and natural gas are significant fossil fuels and feedstocks for chemical production. The price of oil and natural gas rely on its supply and demand, which depends on the global business cycle and unexpected situations. According to a record in mid-2003 and mid-2008, the WTI (West Texas Intermediate) crude oil price went from $28/barrel to $134/barrel because of demand mainly driven by Asian markets. However, the global recession dropped the oil price down to $39/barrel in February 2009. Following this drop, the price increased until July 2014 before falling again as a consequence of the unexpected growth of U.S. shale gas[1]. It is clearly seen that oil price fluctuates and is difficult to predict. The natural gas price has been inconsistent too.

Currently, the shale gas boom causes a great impact on the chemical industry. This growth not only causes oil and natural gas prices to swing, but it also creates both opportunities and challenges of value-added shale gas supply chain. Shale gas provides a supply of natural gas and natural gas liquid, and the shale gas growth has consequently caused the natural gas price to drop, affecting chemical price production costs. The U.S. chemical industry benefited most from this trend as it changed its position in the market from the world’s highest-cost producer in 2005 to lowest-cost producer in 2015[3]. Following this trend, it can be forecasted that manufacturing from shale gas will be prosperous. While this is enticing, it must be recognized that shale gas is a nonrenewable resource and the reliance on natural gas from shale gas as a feedstock will lead to shale gas shortages, causing the price of shale gas to be higher and increase downstream production cost.

Due to uncertainty and price fluctuations of chemicals including oil and natural gas, society has started looking for alternative sources for chemical production that are both economical and sustainable to be able to withstand highly fluctuating fossil fuel price environment. Bio-based production is an interesting alternative option as it reduces carbon emission and effect of global warming which is a major environmental concern. It is expected that biomass-based routes will make a worthwhile impact on the chemical production within 10-20 years[5].

Following through the shale gas revolution, a shift from naphtha cracking to ethane cracking has occurred. As the amount of propylene from ethane cracking is less than propylene from naphtha cracking, the propylene in the market is inadequate[6]. The inadequacy of propylene in the market is confirmed by US Energy Information Administration (EIA) weekly statistics which reports that the US propylene supply in 2016 has been reduced about 40-50% from 2015[7]. The shortages of propylene along with the rapid growth in propylene-based products cause propylene price to be higher. Due to the propylene supply and price trend, there is motivation to study numerous options to produce propylene or propylene based-products.

1.2 Isopropanol

Isopropyl alcohol is a clear liquid which has an alcoholic odor. It is also called isopropanol, 2-propanol, or propan-2-ol. It is miscible in water and ethyl alcohol. It strongly reacts with oxidants. Isopropanol is a precursor of methyl isobutyl ketone (MIBK), isopropylamines, and isopropyl ester[8].

Isopropanol is one of the most widely used solvents in the world. It is used in various field including households, cosmetic and personal care products, pharmaceuticals, veterinary, electronics, and automotive industry. Isopropanol is categorized into grades based on its applications. For the industrial grade, it can be used as extraction solvents, carrier solvents, detergents, surface coatings, paints and inks, pesticide formulations, resins and household cleaners. For the cosmetic grade, it can be used as personal care products, rubbing alcohol, and antiseptics. For the pharmaceutical grade, it can be used as a solvent in drug/capsule manufacture, medical wipes, and medical formulation. For the electronic grade, it can be used as drying agents and cleaner for printed circuit boards, flat panel displays, and other electronic devices[9]. Isopropanol can also be applied as antifreeze agents, coupling agents and polymerization modifiers[8]. Beyond these graded applications and uses, isopropanol has other industrial applications too. For instance, isopropanol can be used as a coolant in beer manufacture, and a motor oil from low-graded isopropanol[8]. Additionally, it can be used in acetone production. However, according to IHS Markit[10], isopropanol application as the production of acetone has decreased to less than one percent in 2014. This is likely due to the growth of phenol production. Acetone is a coproduct of phenol production so an increase in phenol simultaneously presents an increase in acetone.

1.3 Isopropanol manufacture

There are three commercial routes to produce isopropanol. These routes are indirect hydration of refinery-grade propylene, direct hydration of chemical-grade propylene, and hydrogenation of acetone.

1.3.1 Indirect hydration

Indirect hydration is a two-step reaction process converting propylene to isopropanol. The reactions are esterification and hydrolysis. The indirect hydration process, also called a sulfuric acid process, uses sulfuric acid as a solvent. This method is known as the first commercial process of isopropanol production. Its conversion is very high (conversion=93%), and its selectivity to isopropanol and its main byproduct (diisopropyl ether, DIPE) is above 98%[12]. Stoichiometric equations of this process are provided in Table 1.

Table 1 Chemical reactions of indirect hydration process

Step1. Esterification[12]	
Main reaction	$CH_3CH = CH_2 + H_2SO_4 \leftrightarrows (CH_3)_2CHOSO_3H$ $(CH_3)_2CHOSO_3H + CH_3CH = CH_2 \leftrightarrows ((CH_3)_2CHO)_2SO_2$
Step2. Hydrolysis[12]	
Main reaction	$(CH_3)_2CHOSO_3H + H_2O \leftrightarrows (CH_3)_2CHOH + H_2SO_4$ $((CH_3)_2CHO)_2SO_2 + 2H_2O \leftrightarrows 2(CH_3)_2CHOH + H_2SO_4$
Side reaction	$(CH_3)_2CHOSO_3H + (CH_3)_2CHOH \leftrightarrows ((CH_3)_2CH)_2O + H_2SO_4$ $((CH_3)_2CHO)_2SO_2 + (CH_3)_2CHO \leftrightarrows (CH_3)_2CHOSO_3H + ((CH_3)_2CH)_2O$

It can be seen from the stoichiometric equations that there is sulfur in both reactions. So, the industries that use the indirect hydration method must use sulfur-resistance materials and consider corrosion problems. It is reported that all of the isopropanol manufacturing plants in the United States, such as Exxon, Shell, and Union Carbide Chemicals, use this method to produce isopropanol even though this method requires high energy for acid reconcentration and causes environmental problems[12, 13]. The environmental problems come from the disposal of water, sulfuric acid, spent soda, and off-gas waste[13]. The reason for the industry to select this process may be that this process requires low-purity propylene feed, which is 40-60 wt%[12]. Therefore, the industries can minimize their raw material costs.

The indirect hydration process can be divided into two sub-processes according to a sulfuric acid concentration used in the process. The process with a high sulfuric acid concentration (more than 80 wt%) is called a strong acid process. This process operates at low temperature and pressure (T = 293-303 K, P = 10-12 bar) and requires stainless steel as the material of construction to avoid corrosion problems from a high concentration of sulfuric acid. Another process is a weak acid process or a process with a low sulfuric acid concentration (60-80 wt%). This process occurs at higher temperature (T = 333-338 K). The weak acid process can minimize the cost of reconcentration and corrosion problems as it requires lower sulfuric concentration[12].

1.3.2 Direct hydration

Direct hydration process is a process converting propylene to isopropanol via a single-step reaction, propylene hydration. It is a general process that is used in Europe and Japan[14]. This method is different from the indirect hydration process as this process operates at high temperature and high pressure in order to improve the effectiveness of the reaction. Although this process deals with a high-pressure condition, it has some significant advantages over the indirect hydration process. The direct hydration process uses water as a solvent instead of a sulfuric acid. Therefore, it does not have corrosion and environmental problems from an acid solution. However, the main hindrance of this method is that the process requires high-purity feed (at least 90 wt% propylene)[12]. The stoichiometric equation of the propylene hydration process is provided below.

$$CH_3CH = CH_2 + H_2O \leftrightarrows (CH_3)_2CHOH$$

Similarly, the main byproduct of this process is diisopropyl ether (DIPE). There are three types of processes based on the reaction phase of the direct hydration. It is noted that all of them are commercial processes and each type of process has its own advantages and disadvantages. Table 2 summarizes conditions of different processes.

Table 2 A summarize of direct hydration processes

Process	**Vapor phase**	**Mixed vapor-liquid phase**	**Liquid phase**
Manufacture	Veba-Chemie	Deutsche Texaco	Tokuyama Soda
Propylene feed (wt%)	99	92	95
Temperature (K)	513-533	403-433	543
Pressure (bar)	26-65	80-100	200
Catalyst	Phosphoric acid on carrier	Ion exchange resin	Tungsten
Catalyst regeneration	No	No	Yes
Conversion	5-6% propylene	75% propylene	60-70% propylene
Isopropanol selectivity	96%	93%	98-99%

According to the summarized table, the conversion of the vapor phase process is very low, which tends to not be economical. This process will not be able to compete with other processes because it needs high-pressure requirements and gas recycle[12]. In addition, it is reported that the catalyst lifetime in the mixed vapor-liquid phase process is short[12]. Therefore, the process in the mixed vapor-liquid phase will lose benefits to the liquid phase process. In the final conclusion, the liquid phase process is the most interesting process for producing isopropanol by the direct hydration method.

1.3.3 Acetone hydrogenation

Acetone hydrogenation process is the most recent technology of isopropanol production. The reaction can be done by mixing acetone and hydrogen in the presence of a fixed catalyst bed. An example of an appropriate catalyst for the acetone hydrogenation is Rayney catalyst. The conversion and selectivity of this process are extremely high. While the conversion is 99.9%, the selectivity equals 99.99%[13]. Even though the acetone does not need to be pure, the reaction is preferable when the water content in the acetone feed is between 1.2-4 wt% based on solution of water and acetone. It is reported that adding water in the feed can improve the yield of isopropanol. However, it increases the amount of byproduct in the process so that a large amount of energy is required for the additional separation process to purify isopropanol. Balancing its benefits and drawbacks, extra water in the feed will lead to an adverse economic condition[15].

1.3.4 Other processes

Beyond these conventional routes, there are many ways to produce isopropanol from different chemicals. The examples include oxidation of propane, transesterification of isopropyl acetate, and fermentation. As there are many pathways other than the conventional methods, it is important to investigate other possible routes for an advantage of feedstock availability.

1.4 Isopropanol market

The global isopropanol market has been growing over the past few years. Its compound annual growth rate (CAGR) is approximately seven percent with global demand growth of two percent[10, 16]. The reason for the moderate demand growth is because of the environmental regulations on volatile organic compounds in Europe and North America. However, the market growth rate is expected to be greater in the future owing to the potential of the pharmaceutical market in Asia-Pacific region, especially in China and India. It is important to note that the demand for isopropanol Asia-Pacific accounts for 39.6% of the isopropanol global demand and it is expected to rise[16]. Despite the increasing demand, the price is decreasing. The market price of isopropanol is approximately \$0.6/lb in 2015 but dropped to \$0.34-0.36/lb in 2016. According to the ICIS, the isopropanol price in 2016 is the lowest price during past seven years due to the low price of the propylene feedstock[17]. However, the price is expected to rise because of predicted demand.

Experts believe that expansion of pharmaceutical and household industry will push the potential of the isopropanol market up. The global pharmaceutical growth is estimated to be over five percent from 2013 to 2018, signaling for the growth of the isopropanol market[18]. An improvement in motor oils and automotive industry can also raise isopropanol demand[8].

2. PROBLEM STATEMENT

The price of propylene is expected to increase as a result of shale gas revolution. Therefore, it is imperative to find alternative pathways to produce propylene derivatives for a long-term, cost-effective, and sustainable production. One of the most attractive chemicals from propylene is isopropanol because of its high demand growth and wide applications. The objective of this research is to determine alternative pathways for isopropanol production, select the possible routes using MISR as an economic indicator, and select the most sustainable pathway through a techno-economic analysis.

In this research, it is specified that a superstructure covers all possible pathways, including experimental processes. The number of synthesis per route is limited to a two-step maximum from the product. In addition, for an economic analysis, a 30% tax rate and a ten-year linear depreciation are assumed to calculate the return on investment (ROI). It is noted that the catalyst cost was not included in the cost calculation.

This research will allow industry to have more choices when they want to produce isopropanol in complex situations and can choose the pathway corresponding to their feedstock availability. Furthermore, it provides the most economical way to produce isopropanol, which will be beneficial to chemical industries who want to start or improve the production in the future.

3. METHODOLOGY

Many steps were taken to determine the optimal pathway for sustainable isopropanol production. These steps included generating a superstructure of alternative pathways, screening for potential pathways, creating a synthesis and simulation of flowsheet, performing an economic analysis, and selecting the best pathway. For clarity, Figure 1 illustrates the required research steps of a techno-economic analysis. The following subsections provide additional details on these steps.

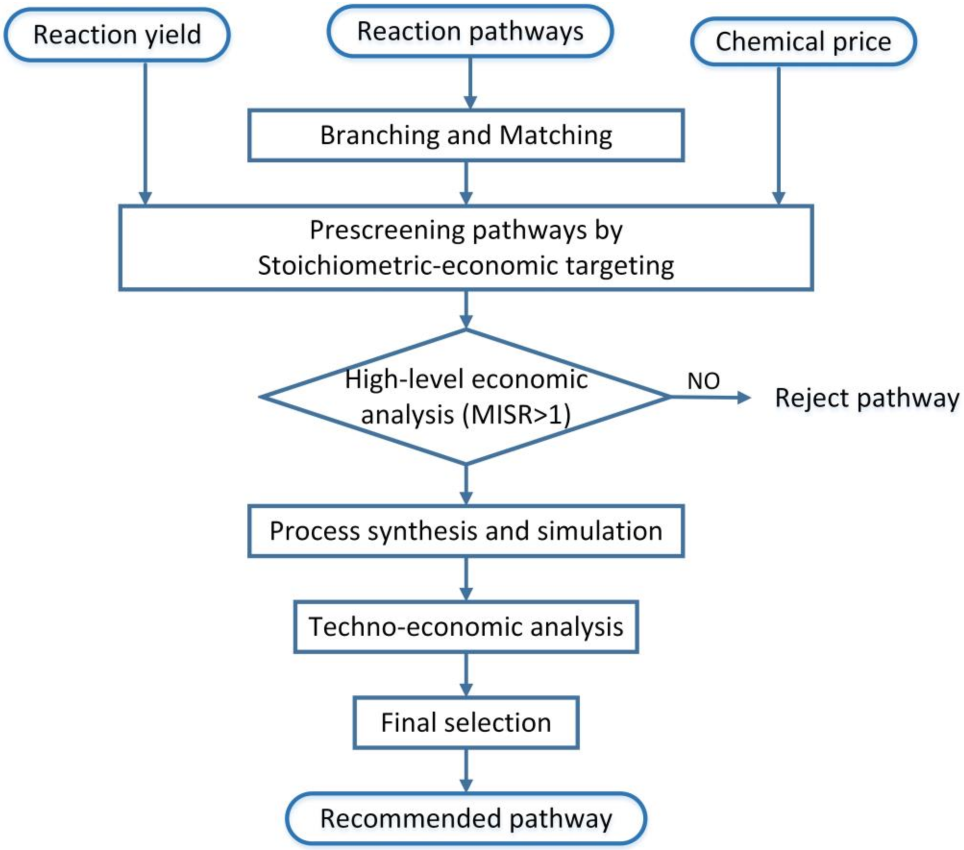


Figure 1 Methodology diagram

3.1 Generating a superstructure of alternatives

According to the steps in the methodology, the first step was creating a superstructure of alternative ways to produce isopropanol. The superstructure was constructed based on a branching, matching and interception approach.

3.1.1 Branching

Branching is a strategy of gathering all of the pathway information by associating the chemicals with sources and main products. The branching approach can be achieved from either a forward branching or a backward branching. The forward branching is a method for searching intermediates from feedstocks by forward approach. For example, in forward branching biomass is a source of methanol, ethanol, etc. Likewise, the backward branching is a method for searching intermediates from products by backward approach. For example, as a backward approach isopropanol is made from propylene, acetone, propane, etc[19]. For a better understanding, the branching approach is demonstrated in Figure 2. An example of branching approach which is the branching approach for isopropanol production is also shown in Figure 3.

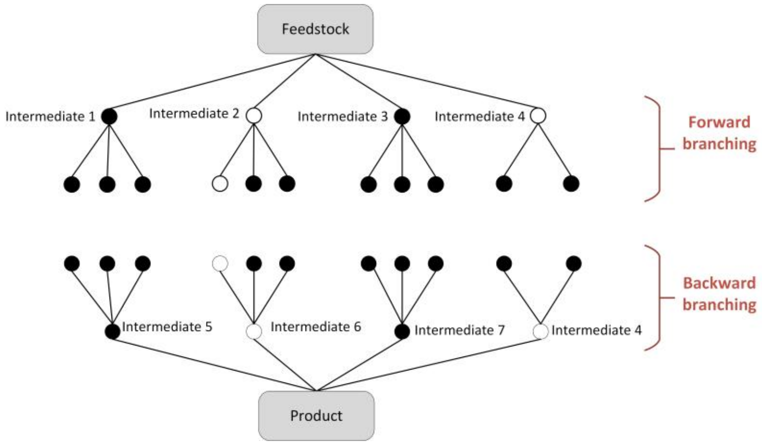


Figure 2 Branching approach
(Adapted from Pham, V. and M. M. El-Halwagi, "Process Synthesis and Optimization of Biorefinery Configurations", AIChE J., 58(4), 1212-1221 (2012))

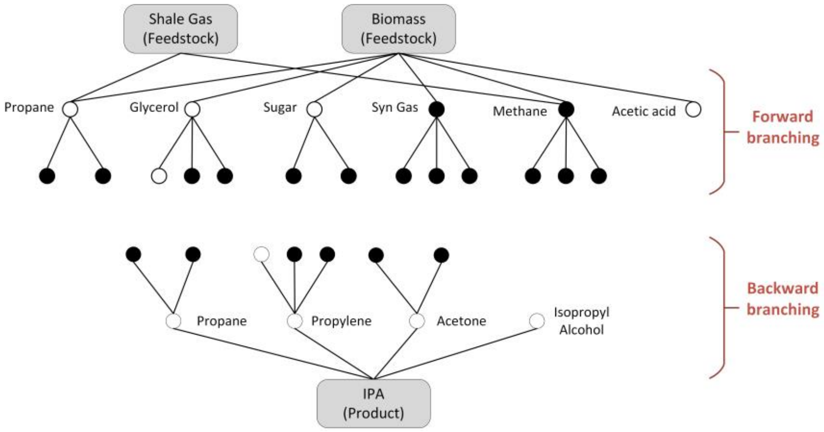


Figure 3 Branching approach for isopropanol production

3.1.2 Matching and interception

After branching the chemicals, connecting those chemicals or intermediates together is needed to form a continuous pathway. When identical chemicals are connected, it is called matching. On the other hand, when different chemicals are connected via chemical reactions, it is called interception[19]. Figure 4 and Figure 5 show the matching approach in general and matching approach for isopropanol production, respectively.

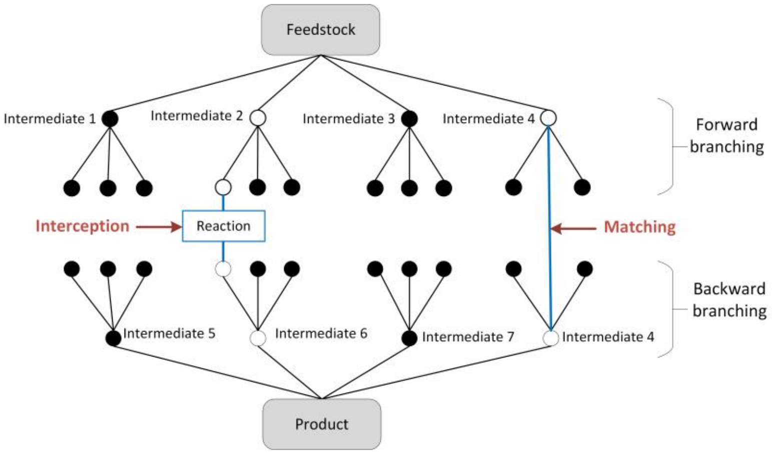


Figure 4 Matching approach
(Adapted from Pham, V. and M. M. El-Halwagi, "Process Synthesis and Optimization of Biorefinery Configurations", AIChE J., 58(4), 1212-1221 (2012))

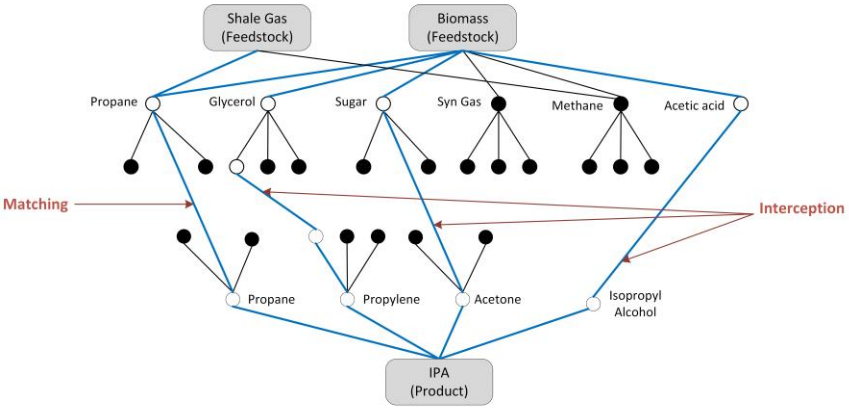


Figure 5 Matching approach for isopropanol production

3.2 Prescreening pathways

After getting the superstructure of alternatives for isopropanol production, the next step was screening the potential pathways in order to provide benchmarks for economic analysis. Metric for Inspecting Sales and Reactants (MISR), an indicator of 'Stoichiometric-Economic Targeting' (Stoichio-nomic) method, was used for the preliminary screening in this research.

MISR is defined as [19]:

$$MISR = \frac{\sum_{p=1}^{N_{products}} F_p \times S_p}{\sum_{r=1}^{N_{reactants}} F_r \times C_r}$$

Where F_p is the annual production rate of product p, S_p is the selling price of product p, F_r is the annual feed rate of reactant r and C_r is the purchase cost of reactant r.

The chemical prices for MISR calculation are listed in Appendix A. This pricing data was obtained from ICIS Chemical Business and https://www.icis.com/chemicals/channel-info-chemicals-a-z/.

A pathway that should be deliberated for detailed analysis is a pathway that has a minimum MISR value of 1. It should be noted that a pathway that has value of MISR slightly more than 1 should not be considered as this MISR value does not include additional process costs such as reaction conversion losses, fixed cost, and operating cost of the processes.

Besides the Stoichio-nomic method, additional information of reactions from publications was considered in order to improve the screening performance. Unpromising pathways included the routes with low-yield reactions and the routes with low-conversion reactions. This research also excluded routes that had the interested chemical as a coproduct or byproduct of the reaction because the interested chemical productivity would be insufficient to reach market demand. Furthermore, publications that compared different methods for converting the same feed to the same product were also applicable to this research. The most efficient method was selected as the best pathway in the final superstructure.

In case where more than one pathway that had the same feed and same product, but had different number of routes, a pathway that contained the least number of routes was selected.

3.3 Synthesis and simulation of flowsheet

Simulation flowsheets were created based on the results from prescreening step. The program selected for process simulation was Aspen Plus. Some important information was needed to be examined to run the simulation such as reaction conversion, product specification, and operating condition. It is noted that this research simulated only base-case scenario, and the existing processes in the publications were not simulated.

3.4 Techno-Economic analysis

Following the simulation part, an economic analysis was performed to evaluate feasible pathways. The analysis was carried out by hand-calculation and Activated Economics in Aspen Plus, which accounted for capital investment and operating cost in its calculation. The return on investment (ROI) was used to evaluate the efficiency of an investment on each process.

A total capital investment (TCI) is a cost associated with starting up a chemical plant, which is a combination of a fixed capital investment (FCI) and a working capital investment (WCI). The fixed capital investment in this research included equipment costs, installation expenses, engineering costs, and contingency charges. The FCI in the cost estimation is equal to five times of a total purchased equipment cost according to *Sustainable design through process integration*[19]. A working capital investment is the amount of money needed to pay for an unexpected plan or stock-pilling raw materials before production. The working capital is usually equal to 10-25% of TCI, depending on a project's size[20]. This research estimated the working capital to be 15% of TCI.

An operating cost is an expense associated with production. Total operating cost can be broken down into two categories: a fixed operating cost and a variable operating cost. A fixed operating cost is an operating expense that is independent of the production line. The fixed operating cost in this research included salaries and wages, maintenance costs, property taxes and insurances, plant overheads. Additionally, a variable operating cost is an operating expense that depends on the production line. In this research, the variable operating cost included raw materials costs, utilities costs, and waste disposal costs[20]. It should be noted that the catalyst cost was not included in this economic analysis.

Even though it is called techno-economic analysis, environmental and safety concerns were not neglected. This research also considered laws and regulations from The United States organizations such as Environmental Protection Agency (EPA), Occupational Safety and Health Administration (OSHA). It is significant to note that the industries must not trespass those regulations to avoid any negative circumstances. The costs of air control and wastewater treatment were taken into account for process cost evaluation. These treatment costs were added to the fixed capital or operating cost, depending on treatment cases. For example, a wastewater treatment cost was included in the operating cost, a pollution control equipment cost was included in the fixed capital investment. In this research, the treatment methods and their cost estimations were obtained from EPA Air Pollution Control Cost Manual[21].

An economic comparison of alternative pathways was performed using a return on investment (ROI) as a profitability criteria. ROI is a simple tool to determine a project profitability without considering interest or the time-value of money.

Rate on investment is defined as[19]:

$$ROI = \frac{Annual\ net\ (After - tax)\ profit}{TCI} \times 100\%$$

Where $Annual\ net(After - tax)\ profit =$

$$(Annual\ income - Annual\ operating\ cost - Depreciation) * (1 - Tax\ rate) + Depreciation$$

In this calculation, a 30% tax rate and a ten-year linear depreciation were assumed.

3.5 Final selection

The process with the highest value of ROI was the most attractive pathway. However, it should be noted that the margin of error in this calculation was about 10-20%. So, if the difference of ROI values of processes was in the range of error, a sensitivity analysis of the processes was perform to assess the impact of feedstock price on the ROI of processes. The process with a low impact of the feedstock price was selected as the most promising pathway.

4. RESULTS AND DISCUSSIONS

4.1 Superstructure of alternatives

The superstructure of isopropanol production resulting from branching, matching and interception is demonstrated in Figure 6. The definition of chemicals and conversion technologies are also described in Table 3 and Table 4. It should be noted that this research considered all possible reactions and processes which included theoretical reactions, laboratory processes, and commercial processes.

Table 3 Chemical names of isopropanol production

Alphabet	Chemical name	Alphabet	Chemical name	Alphabet	Chemical name
A	Naphtha	H	Ethanol	O	Butane
B	Biomass	I	Propane	P	Benzene
C	Sugar/ Carbohydrate	J	Propanol	Q	Acetic acid
D	Syngas	K	Methanol	R	Propylene
E	Methane	L	Acetylene	S	Acetone
F	Ethane	M	Ethylene	T	Isopropyl acetate
G	Glycerol	N	Acetaldehyde	U	Isopropanol

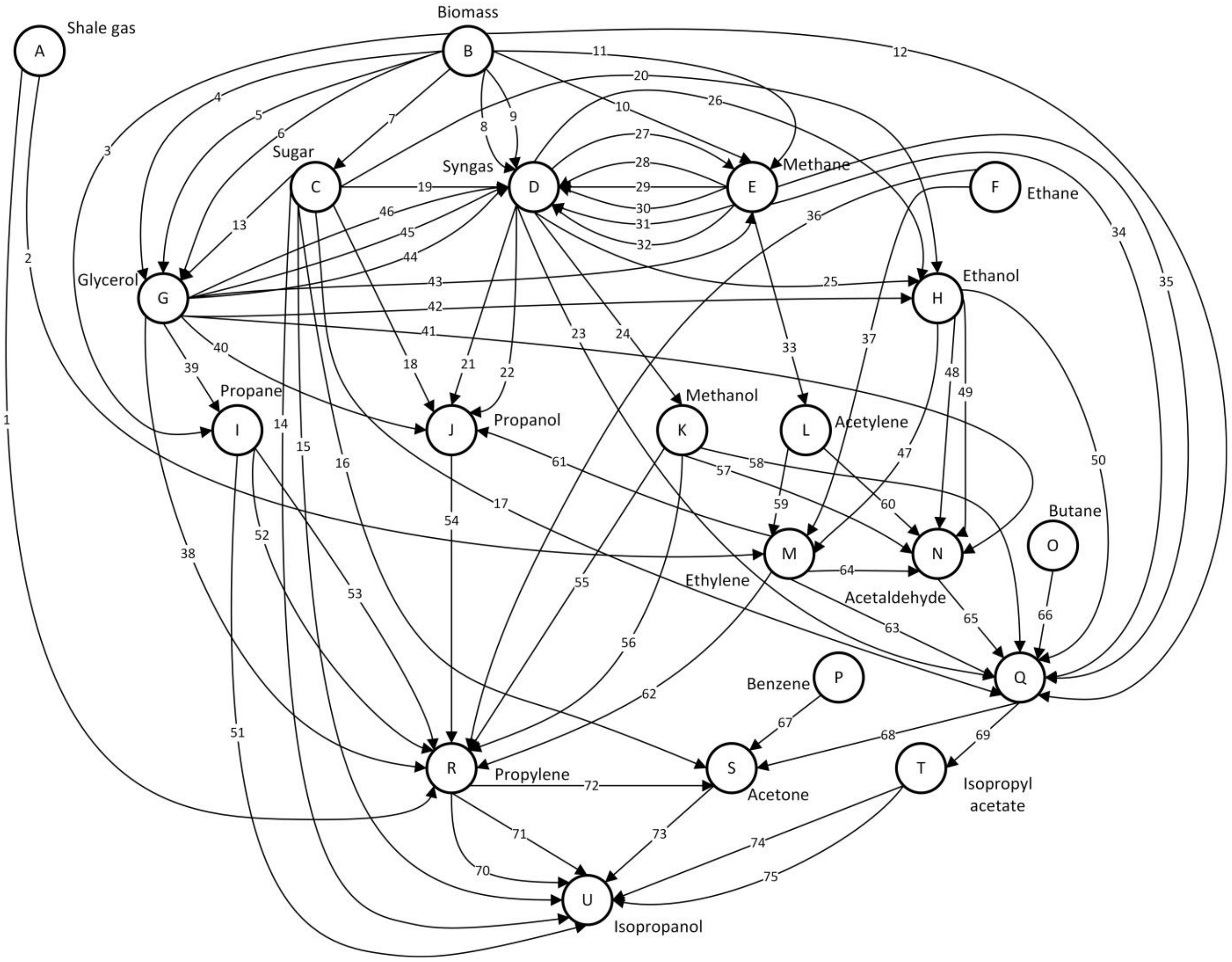


Figure 6 Pathways for isopropanol production

Table 4 Technology legend of isopropanol production

Number	Conversion technology	Number	Conversion technology
1	Fluid catalytic cracking[22]	21	Syngas fermentation[23]
2	Fluid catalytic cracking[22]	22	CO hydrogenation[24]
3	Hydrogenation[25]	23	CO hydrogenation[24]
4	Transesterification[26]	24	CO hydrogenation[24]
5	Saponification[26]	25	Syngas fermentation[23]
6	Hydrolysis[26]	26	Methanation[24]
7	Hydrolysis[19]	27	CO hydrogenation[27]
8	Pyrolysis[27]	28	Stream reforming[28]
9	Gasification[27]	29	Autothermal reforming[28]
10	Landfill[19]	30	Dry reforming[28]
11	Digestion[19]	31	Combined reforming[28]
12	Pre-hydrolysis[29]	32	Partial oxidation[28]
13	Fermentation[30]	33	Pyrolysis[31]
14	IB, IBE Fermentation[32]	34	Carbonylation[33]
15	Cellobiose degradation[34]	35	Oxidative bromonation[35]
16	ABE Fermentation[36]	36	Stream cracking[37]
17	Hydrothermal[38]	37	Stream cracking[37]
18	Fermentation[32]	38	Hydro-deoxygenation[39]
19	Gasification[27]	39	Hydro-deoxygenation[39]
20	Fermentation[40]	40	Hydrogenolysis[41]

Table 4 Continued

Number	Conversion technology	Number	Conversion technology
41	Pyrolysis[42]	59	Hydrogenation[43]
42	Fermentation[44]	60	Hydration[45]
43	Anaerobic digestion[44]	61	Hydroformylation and Hydrogenation[13]
44	Pyrolysis[30]	62	Metathesis[22]
45	Gasification[30]	63	Vapor phase oxidation[33]
46	Stream reforming[30]	64	Oxidation (Wacker Process)[45]
47	Dehydration[46]	65	Oxidation[33]
48	Dehydrogenation[45]	66	Oxidation[33]
49	Oxidation[45]	67	Cumene and Hock Process[36]
50	Oxidation[47]	68	Ketonization[48]
51	Direct oxidation[49]	69	Esterification[50]
52	Dehydrogenation[51]	70	Indirect hydration[13] (esterification+hydrolysis)
53	Oxidative dehydrogenation[51]	71	Direct hydration[13]
54	Dehydration[41]	72	Oxidation[36]
55	MTP Process[52]	73	Hydrogenation[13]
56	MTO Process[52]	74	Transesterification[53]
57	Hydroformylation[45]	75	Hydrolysis[54]
58	Carbonylation[33]		

4.2 Prescreening pathways

Applying the Stoichio-nomic method with the MISR as an indicator for elimination, the following routes were eliminated: transesterification of isopropyl acetate (74), hydrolysis of isopropyl acetate (75), ketonization of acetic acid (68), dehydration of 1-propanol (54). These eliminated routes also affected routes that they connected to. The effected routes are listed in Table 5. The numbers in Table 5 represent the technology legend listed in Table 4.

Table 5 A summary of affected routes from elimination process

Eliminated routes	Affected routes
74, 75	69
68, 69	12, 17, 23, 34, 35, 50, 58, 63, 65, 66
65	41, 48, 49, 57, 60, 64
54	18, 21, 22, 40, 61
61, 62, 64	2, 37, 47, 59
59, 60	33
47, 48, 49	20, 25, 26, 42

Reaction data was considered for further elimination. Table 6 presents routes that were removed from the superstructure because of specific reasons corresponding to the publications. Those reasons are also described in Table 6.

Table 6 Eliminated routes with reasons from publications

Route	Feed	Product	Reason
51 Direct oxidation	Propane	Isopropanol	Although the MISR value is about 2.13, the reaction need tert-butyl hydroperoxide (TBHP) as a solvent to maximize its conversion. Because this solvent reacts with the feed, the cost of TBHP should be included in the MISR calculation. An expensive price of TBHP makes this route infeasible.
14 Fermentation 15 Cellubiose degradation	Sugar/ Carbohydrate	Isopropanol	The low-yield conversion of sugar into alcohol

Table 6 Continued

Route	Feed	Product	Reaso
16 Fermentation	Sugar/ Carbohydrate	Acetone	The amount of acetone product is low comparing to the amount of butanol, its coproduct. In addition, the price of butanol is higher than the price of acetone. So, it is more economical if using this technology to produce butanol instead of acetone.
53 Oxidative dehydrogenation	Propane	Propylene	The MISR value of this route is less than the MISR value of route 52. Thus, the propane dehydrogenation in route 52 has higher potential for profitability.

Table 6 Continued

Route	Feed	Product	Reason
4 Transesterification 5 Saponification 6 Hydrolysis	Biomass	Glycerol	As there are abundant glycerol from biodiesel production, glycerol should be obtained from biodiesel production instead of other routes.
13 Fermentation	Sugar/ Carbohydrate	Glycerol	
3 Hydrogenation	Biomass	Propane	Propane is produced in a small amount in green diesel production. So, this route cannot be a major source of propane.
10 Landfill 11 Digestion	Biomass	Methane	Due to the shale gas boom, obtaining methane from shale gas is the cheapest pathway.
27 Methanation	Syngas	Methane	
43 Anaerobic digestion	Glycerol	Methane	

Like the previous approach, as the routes in Table 6 were removed from the superstructure, the hydrolysis of biomass (route 7) was eliminated because it was affected by route 13, 14, 15, 16, 17, 18, 19, and route 20.

A literature review compared different technologies to produce methane from syngas. Julián-Durán, L.M., et al. performed a techno-economic assessment for methanol production from syngas[55]. The result indicates that partial oxidation is the most suitable route to convert syngas to methane from an economic aspect by using ROI as an indicator. Therefore, route 32 was selected as a viable pathway to convert syngas to methane. Moreover, Jasper, S. and M.M. El-Halwagi reported that producing propylene from methanol by Methanol to Olefins process (MTO process) is more economical than by Methanol to Propylene process (MTP process)[52]. Therefore, route 55 was also excluded from the superstructure. It should be noted that even though propylene is a coproduct in MTO process, MTO is a commercial process and can be controlled to produce more propylene than ethylene[22]. Hence, route 56 was retained in the superstructure.

Combining all elimination results from the prescreening step, the superstructure was modified as shown in Figure 7. This research limited the number of synthesis to be two maximum steps from the product (isopropanol) per route. Therefore, the superstructure’s size was reduced as illustrated in Figure 8.

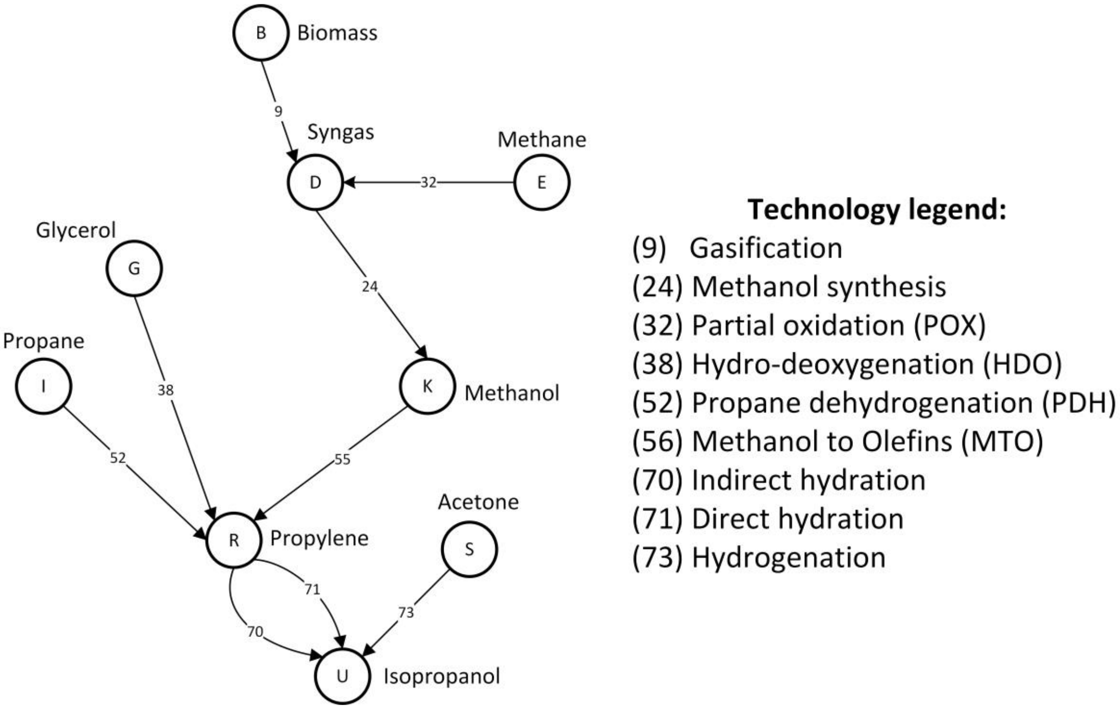


Figure 7 The superstructure of the synthesized pathways from prescreening step

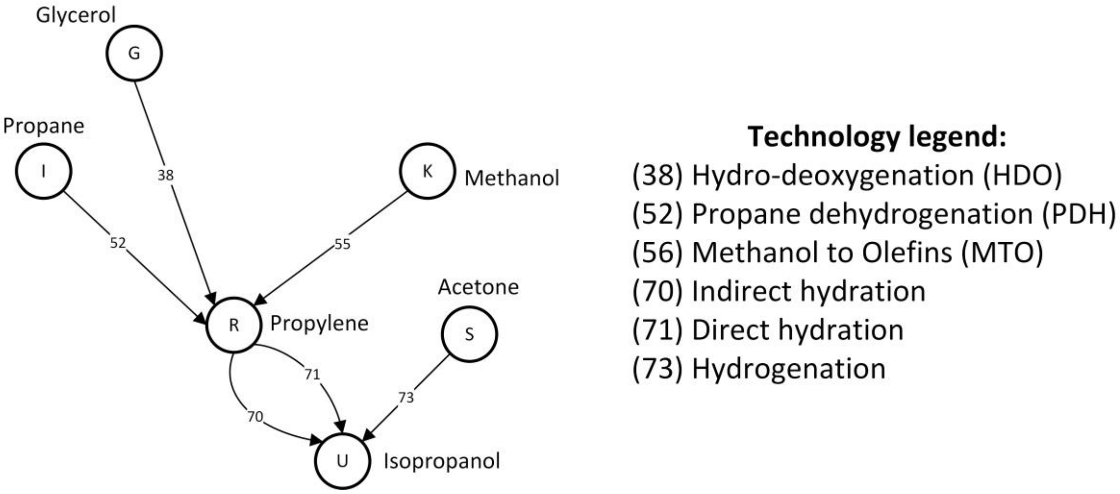


Figure 8 The final superstructure with a two-step maximum from the product

Before performing a techno-economic analysis, the final check for MISR value of each pathway could ensure that these processes had a potential for economic benefit. A summary result of possible pathways with their MISR values is demonstrated in Table 7.

Table 7 Possible pathways result from prescreening step

Nodes	**Feed**	**Product**	**Route**	**MISR**
G → R → U	Glycerol	Isopropanol	Hydro-deoxygenation, hydration	4.67
I → R → U	Propane		Dehydrogenation (PDH), Hydration	3.54
K → R → U	Methanol		Methanol to Olefins (MTO), Hydration	2.52
S → U	Acetone		Hydrogenation	1.74

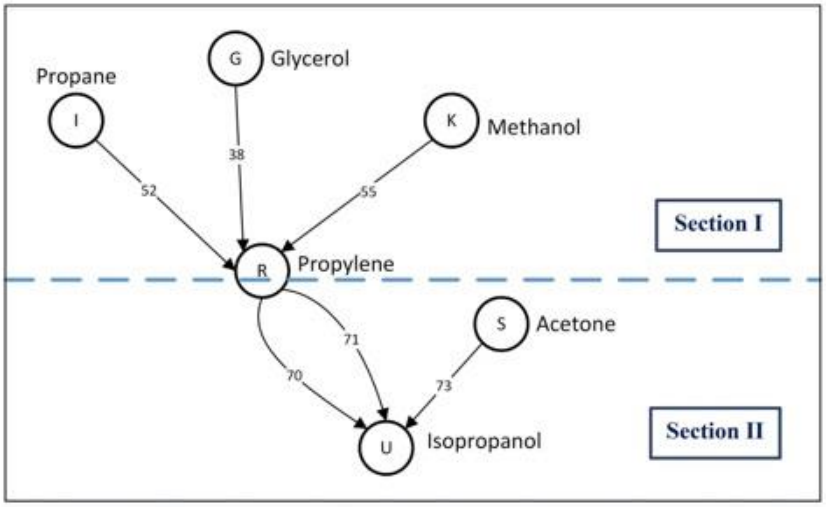


Figure 9 Two sections of the result from the superstructure

For a simplicity, Figure 9 shows the result from the superstructure, which can be divided into two sections. The first section (Section I) includes different routes to produce propylene. Those routes include hydro-deoxygenation of glycerol, dehydrogenation of propane (PDH), and Methanol to Olefins (MTO) process. The second section (Section II) includes different routes for isopropanol production. All of these routes are commercial processes, as previously mentioned in the introduction section. They are indirect hydration of propylene, direct hydration of propylene, and acetone hydrogenation. Therefore, for the final selection, a comparison of different routes to produce propylene and a comparison of different routes to produce isopropanol were performed.

For the comparison of propylene production, cost evaluations of PDH and MTO processes are in the publications. However, a process simulation of the glycerol hydro-deoxygenation has not been created yet. This is because the glycerol hydro-deoxygenation process is still in the experimental stage. Thus, the simulation of the glycerol hydro-deoxygenation reaction was conducted in this research. The simulations were carried out based on the capacity of 350,000 tonnes of propylene per annum.

For the comparison of isopropanol production, even though three viable methods to produce isopropanol in the superstructure are all commercial processes, the economic assessments for each process have not been performed yet. Therefore, three simulation flowsheets for those isopropanol production processes were created. The simulations were carried out based on the capacity of 400,000 of isopropanol per annum.

4.2.1 C3 from biological synthesis

From the superstructure after the prescreening step, it is discovered that none of the processes associated with biomaterials is counted as a possible pathway. The reason behind this is that all C3 fermentation processes have a low yield. It is found that the main limitation of the low-yield fermentation is because of the redox balance and carbon inefficiency. However, this obstacle can be alleviated by knocking out cellular effects with a specific gene[56]. Therefore, the ongoing research in this area is focusing on an engineering fermentation to find the appropriate genes in order to overcome those limitations.

Bio-propylene is a good example of chemical production from biological sources. Rodriguez, B.A., et al. reported that propylene cannot be efficiently produced from sugar under any fermentation conditions[56]. This is because the cost of raw materials cannot compete with the price of product. In other word, sugar price is higher than propylene price. Thus, producers will not get any profit from this process. According to the assessment from Rodriguez, B.A., et al.'s publications, it is predicted that the sugar price should reduce to about $0.13/kg in order to compete with the conventional process[56]. The report provided by Walther, T. and J.M. François also stated that propanol production from the metabolic engineering fermentation still cannot compete with the conventional synthesis even though the current technology is used[32].

4.3 Techno-economic analysis

Based on the results from the prescreening step, a techno-economic assessment of the following processes was performed: glycerol hydro-deoxygenation for propylene production, indirect hydration for isopropanol production, direct hydration for isopropanol production, and acetone hydrogenation for isopropanol production.

This section discusses the technical and economic analysis of these processes. The technical component consists of a process simulation flowsheet and a process description. The economic analysis assesses significant data for cost estimation and economic results. The detailed calculation of each process is described in Appendix C.

4.3.1 Glycerol hydro-deoxygenation

As a general description of the glycerol hydro-deoxygenation has not yet been discussed in this research yet, a brief summary of this process is provided. Glycerol hydro-deoxygenation is a one-step catalytic propylene formation reaction with a conversion of 88% and a selectivity of 76%. A great advantage of this reaction is that propylene is the only product in the gas phase so that the separation section is not required[39]. This process is an enticing process because of its abundance and low-price feedstock. It is worth noting that glycerol is abundant in the market as it is a byproduct from biodiesel production, which has been increasing in recent years[44]. In addition, this process provides an alternative resolution for a problem of surplus glycerol in the market and propylene shortage[41]. However, the main challenge of this process is that the glycerol from the biodiesel industry is crude and impure. Its contaminants, including methanol, salts, and free fatty acids, can damage pipes and equipment[57]. Thus, an expensive glycerol purification technology is required. In this research, the glycerol purification process design was obtained from Duque, J.'s report[58]. Regarding to Zacharopoulou, V.'s study, hydrogen is fed to the process with a molar ratio to glycerol of 53:1[39]. Due to the highly excessive amount of unreacted hydrogen, a hydrogen recovery process was required. A pressure-swing adsorption (PSA) was used to recover hydrogen in the process because it was the most suitable method to purify offgas in the chemical and refining industries[59].

4.3.1.1 Process flowsheet

This process is divided into three sections, which are glycerol pretreatment section, hydro-deoxygenation reaction section, and hydrogen recovery section. The process description and process flowsheet of the pretreatment section are illustrated in *Design and analysis of technological schemes for glycerol conversion to added value products*[58]. In the pretreatment section, raw glycerol, which has a purity of 62 wt%, is purified to a purity of 99.7 wt% before sending to the reaction section. Then, in the hydro-deoxygenation reaction section, glycerol is pump and preheated to the reaction condition before entering the reactor. Hydrogen, another feed, is pressurized and mixed with recycled hydrogen. The combined hydrogen is then preheated to the reaction condition as well. Reactor condition for glycerol and hydrogen are P = 80 bar, T = 573 K. The reactor effluent comes out as the vapor-liquid mixture. The mixture is sent to flash drum which operates at room temperature and atmospheric pressure. The only products in the gas phase are propylene and unreacted hydrogen. The byproducts are all in liquid phase. Therefore, a gas stream of propylene and hydrogen is sent to the pressure-swing adsorption section to purify the propylene product and recycle unreacted hydrogen back to the reaction section. A flowsheet and stream table of the glycerol hydro-deoxygenation process are presented in Figure 10 and Table 10, respectively.

4.3.1.2 Economic analysis

The economic assessment of this process was performed using both the simulation and publications. While the equipment cost for glycerol pretreatment and pressure-swing adsorption (PSA) sections were obtained from the publications, the equipment cost for the reaction section was acquired from the simulation. The total purchased equipment cost was calculated by adding the equipment costs of each section together. A summary of the key information for economic analysis is demonstrated in Table 8 and the economic results of the glycerol hydro-deoxygenation process are shown in Table 9.

Table 8 The key information of glycerol hydro-deoxygenation process

Input/ Output	**Unit**	**Rate**
Raw glycerol (62 wt%)	kt/yr	1,909
Hydrogen	kt/yr	0.112
Refinery-grade propylene (75 wt%)	kt/yr	361
Fuel (from alcohols)	kt/yr	830
Heating utilities	MMBtu/hr	652
Cooling utilities	MMBtu/hr	847
Electricity	kW	638

Table 9 Economic results of the glycerol hydro-deoxygenation process

Description	**Amount (MM$/yr)**
Fixed capital investment (FCI)	388
Total capital investment (TCI)	456
Annual income	349
Annual operating cost	380
Annual ROI	-2 %

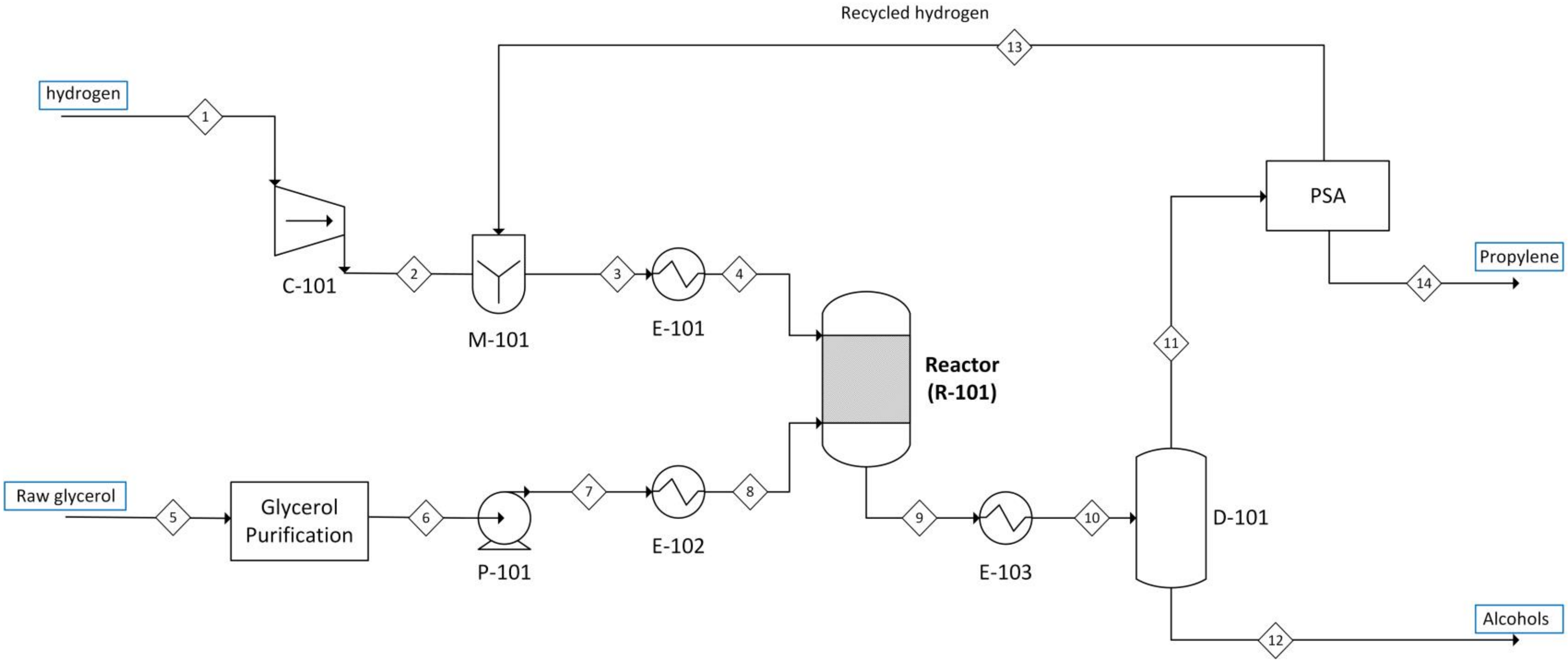


Figure 10 A flowsheet of glycerol hydro-deoxygenation

Table 10 A stream table of glycerol hydro-deoxygenation

Stream Name	**Units**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Temperature	K	323.15	559.065	298.161	573.15	298.15	477.15	478.988	573.15	573.15	298.15	298.15	298.15
Pressure	bar	20	80	80	80	1	1	80	80	80	80	80	80
Mass Flows	kg/hr	7	7	161218	161218	238639	143723	143723	143723	304941	304941	201149	103792
Mass Fractions													
Hydrogen		1.000	1.000	1.000	1.000	0.000	0.000	0.000	0.000	0.512	0.512	0.776	0.000
Propylene		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.144	0.144	0.217	0.002
Methanol		0.000	0.000	0.000	0.000	0.335	0.000	0.000	0.000	0.000	0.000	0.000	0.000
2-Propenol		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.008	0.001	0.022
1-Propanol		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.022	0.022	0.002	0.060
2-Propanol		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.008	0.008	0.001	0.021
Water		0.000	0.000	0.000	0.000	0.000	0.003	0.003	0.003	0.217	0.217	0.004	0.629
Propylene glycol		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.017	0.017	0.000	0.050
1,3 Propanediol		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.017	0.017	0.000	0.050
Glycerol		0.000	0.000	0.000	0.000	0.617	0.997	0.997	0.997	0.056	0.056	0.000	0.166
NaOCH3		0.000	0.000	0.000	0.000	0.027	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Triglycerides		0.000	0.000	0.000	0.000	0.020	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Protein		0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 10 Continued

Stream Name	**Units**	**13**	**14**
Temperature	K	298.15	298.15
Pressure	bar	80	80
Mass Flows	kg/hr	161211	45178.2
Mass Fractions			
Hydrogen		1.000	0.000
Propylene		0.000	0.965
Methanol		0.000	0.000
2-Propenol		0.000	0.003
1-Propanol		0.000	0.008
2-Propanol		0.000	0.006
Water		0.000	0.018
Propylene glycol		0.000	0.000
1,3 Propanediol		0.000	0.000
Glycerol		0.000	0.000
NaOCH3		0.000	0.000
Triglycerides		0.000	0.000
Protein		0.000	0.000

4.3.2 Indirect hydration

4.3.2.1 Process flowsheet

Propylene gas (70 wt% propylene, 30 wt% propane) is fed to the bottom of the absorber reactor to mix with weak sulfuric acid (80 wt% H_2SO_4) from the top of the absorber reactor. In the absorber reactor, propylene is absorbed by the weak sulfuric acid and forms sulfate solution by esterification at the condition of P = 6 bar and T = 363 K. While spent gas is vented out of the process from the top of the absorber reactor, the sulfate mixture from the bottom of the absorber reactor is depressurized and heated before entering the top of the stripper reactor. To form a hydration reaction at streamed pressure with T = 407 K, water and low pressure stream (LP stream) are supplied to the lower section of the stripper reactor. Unreacted sulfuric acid is removed from the bottom of the stripper reactor and recycled back to the absorber reactor for a further esterification reaction. Product from the top of the stripper reactor is fed to the scrubber to neutralize the residual acid with caustic. While spent soda is discharged from the bottom of the scrubber, neutral product leaves the top of the scrubber as vapor stream. The vapor stream is condensed and sent to the drum to separate propylene and propane gases from product stream. The liquid product stream from the drum is pressurized and fed to the first distillation column. The first distillation column operates with the partial condenser. This column separates DIPE and the remaining gas from the product stream. The distillate is sold as fuel. The product stream then enters the isopropanol-water distillation column. As it is an azeotrope distillation, DMSO is used to separate isopropanol from water. Isopropanol with a purity of 99 wt% concentrates in this distillation column as the product stream. The heavy stream from the isopropanol-water distillation column is sent to the last column for separation of water and DMSO. While DMSO is recycled back to the azeotropic distillation column, water is removed from the process as a wastewater. A flowsheet of the indirect hydration process is presented in Figure 11. A stream table of the process is also presented in Table 13.

4.3.2.2 Economic analysis

A summary of the key information from the indirect hydration simulation for an economic analysis is demonstrated in Table 11. The information includes feed flowrates, product and byproduct flowrates, waste flowrates, required utilities, and electricity consumption. As this process discharged waste to environment, a waste treatment cost was included in the profitability calculation. Waste in the process includes sulfuric acid-containing gases, spent soda, and wastewater. After including all of the cost estimation in the economic analysis calculation, the economic results of the indirect hydration process were obtained as shown in Table 12.

Table 11 The key information of indirect hydration process

Input/ Output	**Unit**	**Rate**
Refinery-grade propylene (70 wt%)	kt/yr	452
Stream	kt/yr	161
Sulfuric acid aqueous (80 wt%)	kt/yr	8.58
Caustic soda	kt/yr	96.5
Isopropanol (99.5 wt%)	kt/yr	375
Fuel	kt/yr	35.1
(from DIPE and light gas)		
Vent gases with sulfuric acid	MMft^3/yr	52.6
Process wastewater	MMm^3/yr	0.06
Spent soda	MMm^3/yr	0.289
ESP Wastewater	MMm^3/yr	0.0596
Heating utilities	MMBtu/hr	250
Cooling utilities	MMBtu/hr	285
Electricity	kW	344
Clean water for ESP	MMm^3/yr	0.0015

Table 12 Economic results of indirect hydration process

Description	**Amount (MM$/yr)**
Fixed capital investment (FCI)	135
Total capital investment (TCI)	159
Annual income	497
Annual operating cost	422
Annual ROI	36 %

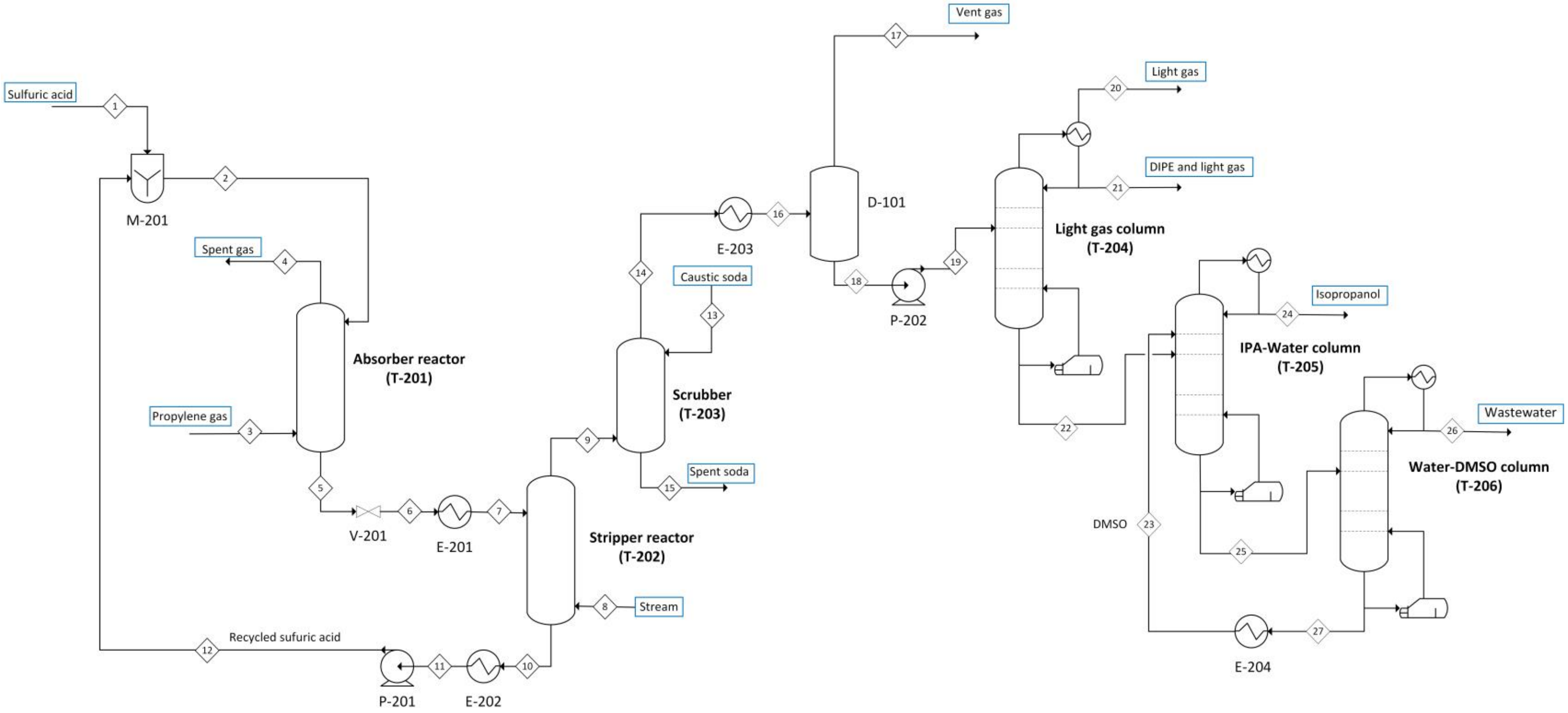


Figure 11 A flowsheet of indirect hydration process

Table 13 A stream table of indirect hydration process

Stream Name	**Units**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Temperature	K	363.15	363.15	363.15	372.469	367.426	342.948	407.15	407.15	405.987	422.452	363.15
Pressure	bar	6	6	6	6	6	1.01325	1.01325	3	1.01325	1.01325	1.01325
Mass Flows	kg/hr	1072	1072	56508.3	1672.86	89697.4	89697.4	89697.4	20170.1	87556.8	63956.3	63956.3
Mass Fractions												
Propylene		0.000	0.000	0.700	0.210	0.027	0.027	0.027	0.000	0.027	0.000	0.000
Propane		0.000	0.000	0.300	0.664	0.177	0.177	0.177	0.000	0.181	0.000	0.000
DIPE		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.014	0.000	0.000
Isopropanol		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.577	0.003	0.003
Diisopropyl sulfate		0.000	0.000	0.000	0.094	0.331	0.331	0.331	0.000	0.000	0.000	0.000
Water		0.200	0.200	0.000	0.032	0.171	0.171	0.171	1.000	0.196	0.048	0.048
Isopropyl hydrogen sulfate		0.000	0.000	0.000	0.001	0.248	0.248	0.248	0.000	0.006	0.000	0.000
DMSO		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sulfuric acid		0.800	0.800	0.000	0.000	0.047	0.047	0.047	0.000	0.000	0.949	0.949
Caustic soda		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sodium bisulfate		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 13 Continued

Stream Name	**Units**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
Temperature	K	363.443	407.15	418.497	407.196	325.337	325.337	325.337	325.554	312.209	312.209	395.221
Pressure	bar	6	1.01325	1.01325	1.01325	1.01325	1.01325	1.01325	5.06625	4.053	4.053	4.32879
Mass Flows	kg/hr	63956.3	12064	85538.4	14531.7	85550.5	18172.1	67378.4	67378.4	3696.35	697.383	62984.6
Mass Fractions												
Propylene		0.000	0.000	0.027	0.001	0.027	0.106	0.006	0.006	0.100	0.024	0.000
Propane		0.000	0.000	0.184	0.005	0.184	0.698	0.045	0.045	0.782	0.228	0.000
DIPE		0.000	0.000	0.014	0.002	0.014	0.008	0.016	0.016	0.113	0.668	0.003
Isopropanol		0.003	0.000	0.582	0.080	0.582	0.159	0.696	0.696	0.002	0.032	0.745
Diisopropyl sulfate		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Water		0.048	0.310	0.192	0.048	0.192	0.028	0.237	0.237	0.003	0.048	0.252
Isopropyl hydrogen sulfate		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
DMSO		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sulfuric acid		0.949	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Caustic soda		0.000	0.690	0.000	0.066	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sodium bisulfate		0.000	0.000	0.000	0.798	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 13 Continued

Stream Name	Units	23	24	25	26	27
Temperature	K	345.15	355.498	423.781	371.364	474.029
Pressure	bar	1.31	1.03421	1.31	1.03421	1.31
Mass Flows	kg/hr	132838	46923.2	148891	16053.1	132838
Mass Fractions						
Propylene		0.000	0.000	0.000	0.000	0.000
Propane		0.000	0.000	0.000	0.000	0.000
DIPE		0.000	0.004	0.000	0.000	0.000
Isopropanol		0.000	0.995	0.001	0.011	0.000
Diisopropyl sulfate		0.000	0.000	0.000	0.000	0.000
Water		0.000	0.000	0.107	0.989	0.000
Isopropyl hydrogen sulfate		0.000	0.000	0.000	0.000	0.000
DMSO		1.000	0.000	0.892	0.000	1.000
Sulfuric acid		0.000	0.000	0.000	0.000	0.000
Caustic soda		0.000	0.000	0.000	0.000	0.000
Sodium bisulfate		0.000	0.000	0.000	0.000	0.000

4.3.3 Direct hydration

4.3.3.1 Process flowsheet

Liquid propylene (95 wt% propylene, 5 wt% propane) is fed to the process and mixed with recycled propylene. The combined propylene stream is pressurized to 152 bar and preheated to 395 K before entering the reactor. Process water is pressurized to 152 bar and preheated to 543 K. Then, propylene and process water react in the liquid phase. The liquid effluent is cooled so that propylene and propane vaporize in a flash drum. The vapor stream from the flash drum is condensed and sent to the propylene-propane distillation column to purify unconverted propylene before recycling it back to the process. Liquid from the flash drum is sent to the separation section to purify the isopropanol product. The separation section consists of three distillation columns. The first column is a partial distillation column, which separates DIPE from isopropanol. Distillate stream from this column is discharged from the process as fuel. The second column is an azeotropic distillation column, which separates water from isopropanol by using DMSO as an extractive solvent. This column purifies the isopropanol product to have 99 wt% purity. The last column is a water-DMSO distillation column, which separates water from solvent in order to recycle water to the feed preparation section and DMSO to the azeotropic distillation column. A flowsheet of the direct hydration process is shown in Figure 12 and a stream table is presented in Table 16.

4.3.3.2 Economic analysis

A summary of the key information from the simulation of the direct hydration process for an economic analysis is demonstrated in Table 14. The information includes feed flowrates, product flowrates, byproduct as fuel flowrate, required utilities, and electricity consumption. Using information from Table 14, the economic results of the direct hydration process are shown in Table 15.

Table 14 The key information of direct hydration process

Input/ Output	Unit	Rate
Chemical-grade Propylene (95 wt%)	kt/yr	350
Process water	kt/yr	101
Isopropanol (99.8 wt%)	kt/yr	326
Fuel (from DIPE and light gas)	kt/yr	82
Heating utilities	MMBtu/hr	495
Cooling utilities	MMBtu/hr	534
Electricity	kW	1,253

Table 15 Economic results of direct hydration process

Description	**Amount (MM$/yr)**
Fixed capital investment (FCI)	195
Total capital investment (TCI)	229
Annual income	432
Annual operating cost	364
Annual ROI	23 %

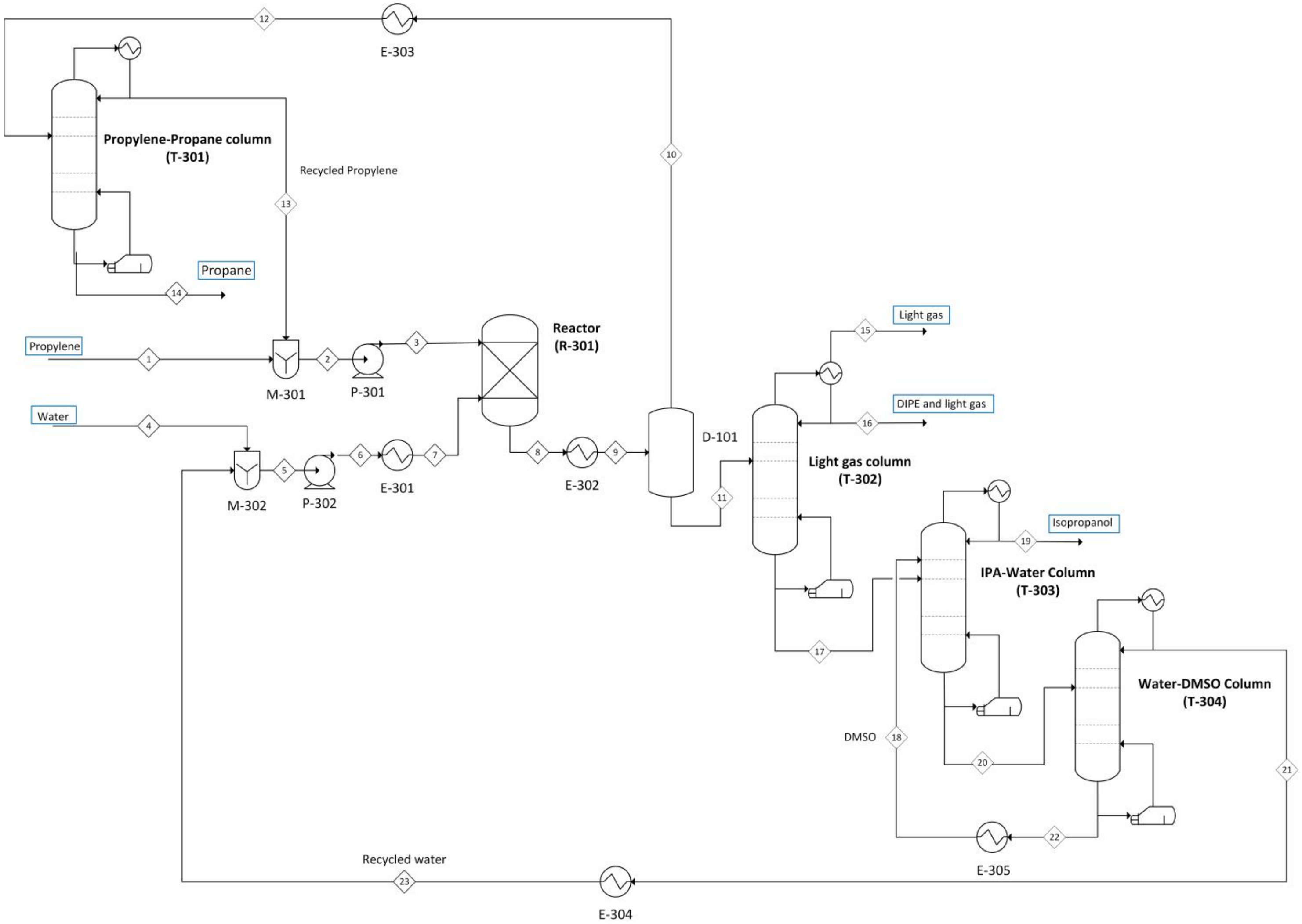


Figure 12 A flowsheet of direct hydration process

Table 16 A stream table of direct hydration process

Stream Name	**Units**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
Temperature	K	315.77	322.96	394.95	308.15	308.15	311.65	543.15	508.30	436.99	437.10	437.10
Pressure	bar	17.51	17.51	151.99	1.01	1.01	151.99	151.99	151.99	151.99	17.37	17.37
Mass Flows	kg/hr	43703.8	54918.3	54918.3	12610.7	50010.4	50010.4	50010.4	104928	104928	16374.8	88553.7
Mass Fractions												
Propylene		0.948	0.754	0.754	0.000	0.000	0.000	0.000	0.118	0.118	0.280	0.089
Propane		0.052	0.046	0.046	0.000	0.000	0.000	0.000	0.024	0.024	0.051	0.019
DIPE		0.000	0.047	0.047	1.000	1.000	1.000	1.000	0.384	0.384	0.158	0.425
Isopropanol		0.000	0.148	0.148	0.000	0.000	0.000	0.000	0.468	0.468	0.495	0.463
Water		0.000	0.005	0.005	0.000	0.000	0.000	0.000	0.006	0.006	0.015	0.004
DMSO		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Stream Name	**Units**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**
Temperature	K	327.79	315.62	445.59	316.04	316.04	403.17	345.15	355.60	416.31	373.74	473.55	308.15
Pressure	bar	17.37	17.24	17.51	5.07	5.07	5.34	1.31	1.03	1.31	1.03	1.31	1.01
Mass Flows	kg/hr	16374.8	5160.17	11214.6	10020.5	226.813	78306.3	221015	40779.4	258415	37399.7	221015	37399.7
Mass Fractions													
Propylene		0.280	0.888	0.000	0.777	0.244	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Propane		0.051	0.112	0.023	0.169	0.064	0.000	0.000	0.000	0.000	0.000	0.000	0.000
DIPE		0.158	0.000	0.231	0.003	0.079	0.480	0.000	0.002	0.145	1.000	0.001	1.000
Isopropanol		0.495	0.000	0.723	0.020	0.462	0.520	0.000	0.998	0.000	0.000	0.000	0.000
Water		0.015	0.000	0.022	0.032	0.151	0.000	0.000	0.000	0.000	0.000	0.000	0.000
DMSO		0.000	0.000	0.000	0.000	0.000	0.000	1.000	0.000	0.855	0.000	0.999	0.000

4.3.4 Acetone hydrogenation

4.3.4.1 Process flowsheet

Hydrogen is fed to the process and pressurized to a pressure of 30 bar. Then, it is mixed with recycled hydrogen and heated to a temperature of 373 K. Acetone is also pressurized and preheated to a pressure of 30 bar and temperature of 373 K. Then, hydrogen gas reacts with liquid acetone in the reactor and gives the vapor-liquid phase product. The mixed-phase effluent is sent to drum to separate vapor from the liquid product. The vapor mixture then enters a cooler to condense all the chemicals but hydrogen. This condensed mixture enters the second drum in order to separate unreacted hydrogen from the mixture. As the liquid mixture from this second drum contains 98.5 wt% of isopropanol, it combines with the liquid product from the first drum in the mixer and leaves the process as a 98.5 wt% isopropanol product. Unreacted hydrogen that leaves the second drum is recycled back to the feed preparation section. Figure 13 and Table 19 presents a flowsheet and stream summary of the acetone hydrogenation process, respectively.

4.3.4.2 Economic analysis

A summary of the key information from the acetone hydrogenation simulation for an economic analysis is demonstrated in Table 17. This information includes input/ output flowrates, required utilities, and electricity consumption. Using information from Table 17, the economic results of the acetone hydrogenation process are shown in Table 18. It should be noted the price of isopropanol in this process was lower than the isopropanol price in other processes because of its lower purity. The price of isopropanol with 98.5

wt% purity was approximated to be $1.2/kg. In addition, similar to the glycerol hydro-deoxygenation process, the cost of PSA unit was taken from the publication.

Table 17 The key information of acetone hydrogenation process

Input/ Output	Unit	Rate
Acetone (98.7 wt%)	kt/yr	359
Hydrogen	kt/yr	20.8
Isopropanol (98.5 wt%)	kt/yr	371
Fuel	kt/yr	11
Heating utilities	MMBtu/hr	7.48
Cooling utilities	MMBtu/hr	0.525
Electricity	kW	884

Table 18 Economic results of acetone hydrogenation process

Description	Amount (MM$/yr)
Fixed capital investment (FCI)	68
Total capital investment (TCI)	80
Annual income	444
Annual operating cost	439
Annual ROI	7 %

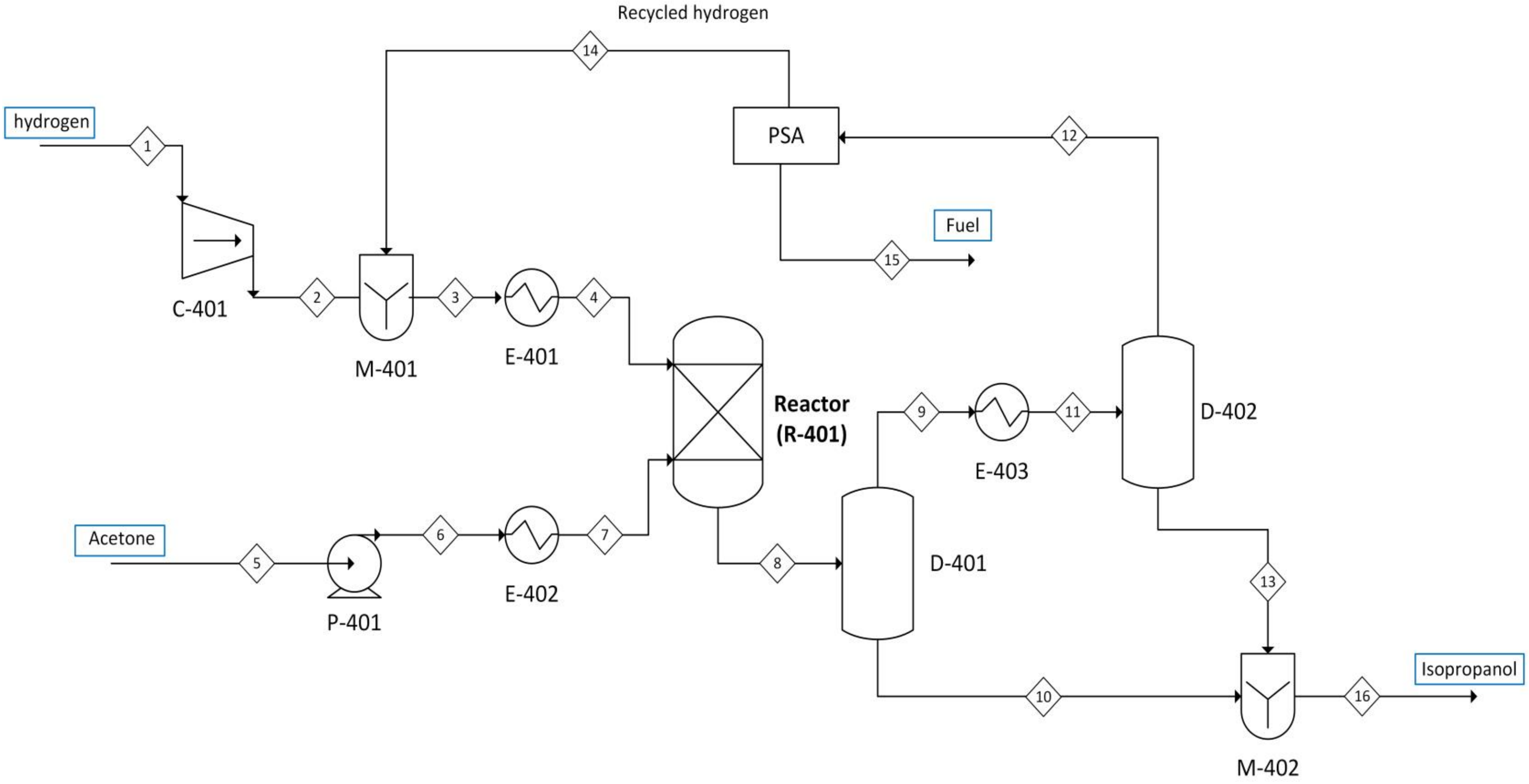


Figure 13 A flowsheet of acetone hydrogenation process

Table 19 A stream table of acetone hydrogenation process

Stream Name	Units	1	2	3	4	5	6	7	8
Temperature	K	323.15	379.782	365.338	373.15	293.15	295.204	373.15	373.15
Pressure	bar	20	30	30	30	1.01325	30	30	30
Mass Flows	kg/hr	2623.95	2623.95	3352.72	3352.72	44876.2	44876.2	44876.2	48228.9
Mass Fractions									
Hydrogen		1.000	1.000	1.000	1.000	0.000	0.000	0.000	0.038
Acetone		0.000	0.000	0.000	0.000	0.987	0.987	0.987	0.001
Isopropanol		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.948
Water		0.000	0.000	0.000	0.000	0.013	0.013	0.013	0.012
2-Hexanol		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001

Stream Name	Units	9	10	11	12	13	14	15	16
Temperature	K	373.15	373.15	313.15	313.15	313.15	313.15	313.15	368.373
Pressure	bar	30	30	30	30	30	30	30	30
Mass Flows	kg/hr	6223.04	42005.9	6223.04	2103.13	4119.91	728.773	1374.35	46125.8
Mass Fractions									
HYDRO-01		0.289	0.000	0.289	0.855	0.000	1.000	0.77851	0.000
ACETO-01		0.002	0.001	0.002	0.002	0.002	0.000	0.00237	0.001
ISOPR-01		0.697	0.986	0.697	0.140	0.981	0.000	0.21405	0.985
WATER		0.012	0.012	0.012	0.003	0.017	0.000	0.00507	0.012
HEXYL-01		0.000	0.001	0.000	0.000	0.000	0.000	5.5E-09	0.001

4.4 Alternatives comparison for final selection

4.4.1 Final selection for propylene production

The viable pathways for propylene production from prescreening step included hydro-deoxygenation from glycerol, propane dehydrogenation (PDH) from propane, and Methanol to Olefins process (MTO) from propane. Regarding to Izadi, M's publication, it is stated that the PDH has more potential to be a profitable process than the MTO[22]. Therefore, the potential pathways after the prescreening step were PDH and glycerol hydro-deoxygenation.

The economic analysis of the PDH process was adapted from Agarwal's publication[60]. Based on the calculation approach of this research, the annual ROI of the base-case design of PDH process was equal to 20%. The key information for economic evaluation of PDH process and its results are presented in Table 20 and Table 21, respectively.

Table 20 The key information of propane dehydrogenation process

Input/ Output	Unit	Rate
Propane	kt/yr	408
Process water	kt/yr	101
Propylene (95 wt%)	kt/yr	350
Hydrogen	kt/yr	30
Heating utilities	MMBtu/hr	1220
Cooling utilities	MMBtu/hr	733
Electricity	kW	21372

Table 21 Economic results of propane dehydrogenation process

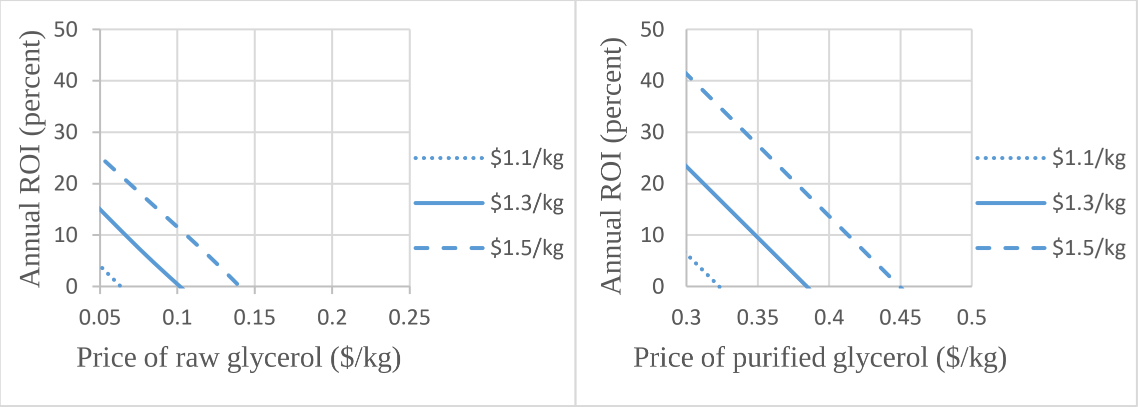
Description	Amount (MM$/yr)
Fixed capital investment (FCI)	430
Total capital investment (TCI)	507
Annual income	363
Annual operating cost	234
Annual ROI	20 %

In respect to the economic analysis of the glycerol hydro-deoxygenation in this research, the annual ROI of the process was negative (annual ROI = -2%). The negative value of ROI indicates that it is not worth to invest in the production of propylene from glycerol via hydro-deoxygenation. Additionally, there are some issues of the glycerol hydro-deoxygenation process. Firstly, the amount of available glycerol in Texas is limited comparing to the amount of required glycerol for propylene production. Biodiesel Magazine reported that the capacity of biodiesel production in Texas is about 395 MMgy (Million gallon per year)[61]. Duque, J. also reported that 1 kg glycerol can be obtained from every 10 kg biodiesel produced[58]. With these two information, it can be estimated that the amount of availabile glycerol from bioidiesel plants in Texas is about 130 ktonnes/year. This number is not high enough to produce 350 ktonnes/year of propylene, which is a propylene-plant nominal capacity in this research. Secondly, this process is still in the experimental stage. There might be some changes in the reaction information and safety issues for the full-scale plant design, which definitely affect the economic results. Due to the reasons above, it can be concluded that the PDH is the best pathway for propylene production.

Although the ROI result of the glycerol hydro-deoxygenation using propylene and raw glycerol market prices is negative, the ROI of this process can be positive if the price of raw glycerol decreases and the price of propylene increases. The sensitivity analysis of hydro-deoxygenation from raw glycerol is shown in Figure 14. When propylene prices are high (more than $1.1/kg), the process can be operate economically with the raw glycerol prices ranging from $0.06/kg to $0.13/kg.

In order to compare the profitability of glycerol hydro-deoxygenation from raw glycerol and from refined glycerol, the sensitivity analysis of the process from refined glycerol was also performed. According to the sensitivity analysis shown in Figure 14, the range of refined glycerol price for economically feasible scenario is between

$0.32-0.45/kg, depending on the propylene selling price. However, it should be realized that the market price of purified glycerol is $0.85/kg and the market price of propylene is in the range of $0.9-1.2/kg. This can be implied that the propylene production from refined glycerol is hardly economically viable because the market price of refined glycerol is about twice the highest feasible price of refined glycerol for the propylene market prices. Therefore, it can be concluded that the propylene production from hydro-deoxygenation of raw glycerol is preferable.

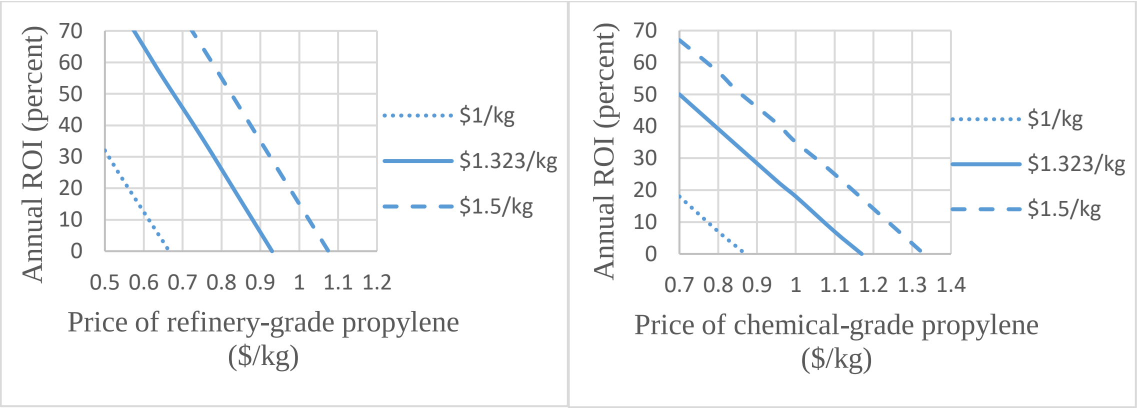


(a) (b)

Figure 14 Sensitivity analysis for the annual ROI of hydro-deoxygenation from raw glycerol (a) and from purified glycerol (b)

4.4.2 Final selection of isopropanol production

According to the techno-economic analyses of indirect and direct hydration processes, the difference of annual ROI values between these processes was about 13%. While the ROI of the indirect hydration was equal to 36%, the ROI of the direct hydration was equal to 23%. As the margin of error in this calculation is about 10-20%, it cannot be fully concluded which pathway is the best pathway to produce isopropanol. So, the sensitivity analyses were performed. The sensitivity analyses of indirect hydration and direct hydration processes are shown in Figure 15. Regarded to the economic analysis of the acetone hydrogenation, the annual ROI was equal to 7%. This annual ROI is significantly small comparing to the ROI values of other isopropanol production routes. Along with the safety consideration of excessive amount of unreacted hydrogen, it can be concluded that the acetone hydrogenation route cannot compete with the other two hydration processes.



(a) (b)

Figure 15 Sensitivity analysis for the annual ROI of indirect hydration (a) and direct hydration (b) processes

The results from the sensitivity analyses show that indirect hydration and direct hydration processes are economically feasible with the isopropanol market price of

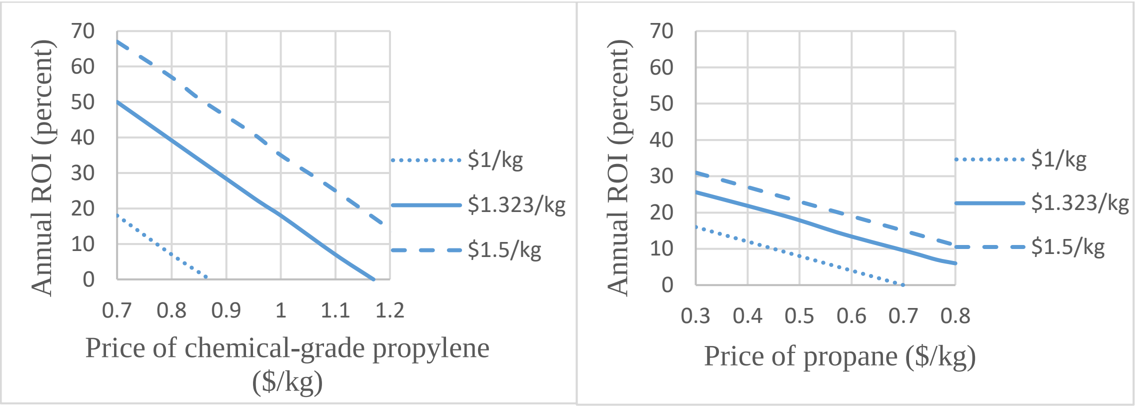
$1.323/kg when the price of the refinery–grade propylene drops below $0.93/kg and the price of the chemical-grade propylene drops below $1.17/kg, respectively. Additionally, when the price of the refinery-grade propylene is reduced to a range of $0.61-1.03/kg, the minimum acceptable level of ROI of the indirect hydration process is achieved. It is noted that the price of propylene for the minimum acceptable level of ROI of the indirect hydration process depends on the product selling price. Similarly, the minimum acceptable level of ROI of the direct hydration process is reached when the price of the chemical-grade propylene is decreased to a range of $0.77-1.24/kg for the different product selling prices. It should be noted that the minimum acceptable level of the annual ROI in this research was equal to 10%. Comparing the impacts of the propylene price to the ROI of indirect hydration and direct hydration processes, the ROI of the direct hydration process is less dependent on its raw material price than the ROI of the indirect hydration process. Therefore, it can be concluded that the direct hydration process is the most attractive method to produce isopropanol.

When considering the direct hydration method as the first candidate for isopropanol production, it is interesting to look into sources of propylene feedstock and make a decision for the most cost-effective approach. It should be noted that the propylene can be obtained by purchasing or manufacturing from the PDH process. In order to make a comparison, the annual ROI of each route was carried out. The annual ROI for the purchasing scenario was taken from the annual ROI of the direct hydration process, which was equal to 23%. For the manufacturing scenario, the annual ROI was calculated based on the economic assessments of direct hydration and PDH processes. The annual ROI for the manufacturing case was equal to 22%. A summary of economic results of purchasing and manufacturing scenarios is presented in Table 22.

Table 22 A summary of economic results of two possible scenarios

Description	**Propylene purchasing scenario**	**Propylene manufacturing scenario**
Fixed capital investment (MM$/yr)	195	625
Total capital investment (MM$/yr)	229	736
Annual income (MM$/yr)	432	462
Annual operating cost (MM$/yr)	364	262
Annual ROI	23 %	22 %

Because these two scenerios had approximately the same value of annual ROI, sensitivity analyses were carried out. Figure 16 shows the ROI trend of each scenerio. According to the sensitivity analyses, the ROI of the purchasing scenerio is more sensitive to the propylene price than the ROI of the manufacturing scenerio to the propane price. Thus, it can be concluded that it is more sustainable to produce isopropanol from propane via PDH and direct hydration processes. The sensitivity analysis of the manufacturing scenerio also reveals that the manufacturing scenerio can operate economically when the propane price is less than $0.95/kg at the isopropanol price of $1.23/kg. Additionally, the minimum acceptable level of ROI (Annual ROI = 10%) for the manufacturing case is achieved with the propane price between \$0.45-0.83/kg, depending on the isopropanol selling price. It should be noted that the sensitivity analysis of the purchasing scenario was duplicated from the sensitivity analysis of the direct hydration process. Thus, the sensitivity results of these two analyses are similar.



(a) (b)

Figure 16 Sensitivity analysis for the annual ROI of (a) propylene purchasing scenario and (b) propylene manufacturing scenario

5. CONCLUSIONS

A superstructure of alternative pathways to produce isopropanol was created. Routes in the superstructure include theoretical reactions, experimental processes, and commercial processes. After unpromising routes were eliminated by using the MISR as an indicator, a superstructure of viable alternatives was obtained. A techno-economic analysis of the following processes was then performed: glycerol hydro-deoxygenation, indirect hydration process, direct hydration process, and acetone hydrogenation process. Economic results with annual ROI values were achieved to determine the most attractive route in each production. The values of annual ROI of processes in this research are listed as following: annual ROI of glycerol hydro-deoxygenation is -2%, annual ROI of propane dehydrogenation is 20%, annual ROI of indirect hydration process is 36%, annual ROI of direct hydration process is 23%, and annual ROI of acetone hydrogenation is 7%. Regarding to the annual ROI results, it can be concluded that the glycerol hydro-deoxygenation cannot outperform the propane dehydrogenation process for propylene production, and the most promising pathway for isopropanol production is the direct hydration process. Even though the annual ROI values of indirect hydration and direct hydration processes do not have much difference, the direct hydration process is more sustainable than the indirect hydration process because its annual ROI is less sensitive to the price of propylene than the annual ROI of the indirect hydration. Additionally, the direct hydration method is preferable when considering corrosion and environmental problems, which are two main problems in the indirect hydration process.

The techno-economic assessments in this research were based from base-case scenarios. Heat integration has not been considered yet. If the integration was included in the analysis, the processes would benefit from savings in cost of utilities and electricity. Therefore, further research could be conducted to improve the potential profitability of the processes.

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APPENDIX A

CHEMICAL PRICES

The chemical prices for the MISR calculation and economic analysis were obtained from publications, ICIS Chemical Business magazines, and ICIS websites. However, most pricing data was acquired from ICIS website. The chemical prices used in this research are listed in Table 23.

Table 23 A list of chemical prices

Chemicals	**Prices ($/kg)**	**Chemicals**	**Prices ($/kg)**
Acetic acid	0.837	Isopropanol	1.32
Acetone	1.08	Isopropyl acetate	1.38
Benzene	1.21	Methanol	0.2
Butanol	1.49	Oxygen	0.025
Butene	0.992	Phenol	1.51
Carbon dioxide	0.05	Process water	0.001
Carbon monoxide	0.075	Propane	0.186
Caustic soda	0.6	Refinery-grade propylene	0.95
Ethanol	0.78	Chemical-grade propylene	0.75
Ethylene	1.27	Propylene glycol	1.33
Glucose	0.4	1-propanol	1.25
Glycerol	0.004	1,3 Propanediol	1.76
Hydrogen	2	Stream	0.01
		Sulfuric acid	0.12

APPENDIX B

PRICES OF UTILITIES

This appendix provides utility prices in order to calculate for the ost of utilities. The utility facilities in the processes in this research include stream, cooling tower water, and electricity. Regarded to a typical cost of utilities from *Sustainable design through process integration*[19], the estimated utility prices are shown in Table 24.

Table 24 Estimated prices of utilities

Energy utility	**Cost**
Heating utility	\$3/ MMBtu
Cooling utility	\$1/ MMBtu
Electricity	\$0.06/ kWh

APPENDIX C

ECONOMIC CALCULATION

In order to perform an economic assessment, a total capital investment and an operating cost were determined. This appendix explains how to estimate these expenses. This appendix is divided into three sections for a better understanding. The first section provides the information and calculation of pollution control expenses. The second and third section describe the calculation of total capital investment and operating cost, respectively.

1. Cost of pollution control

Due to the environmental concern in this research, an environmental expense should be added to the cost estimation of the process that released unpleasant chemicals to the environment. Because the environmental expense can be added to either fixed capital investment (FCI) or operating cost, it is easier to discuss about environmental expense before going into these cost estimations in detail. Looking through the simulated processes, the only process that requires an environmental treatment is the indirect hydration process. Therefore, the cost of pollution control discussed in this section is based on the chemicals released from the indirect hydration process.

According to the indirect hydration process, the required treatments were sulfuric acid-containing gas treatment, spent soda, and wastewater treatment. The sulfuric acid-containing gases included the spent gas discharged from absorber and vent gas discharged from drum. It should be noted that it was assumed that there was a trace of sulfuric acid in vent gas even though the sulfuric acid did not appear in the vent stream in the simulation result. Because the sulfuric concentration in these released gases went beyond the concentration limit from OSHA, the treatment was necessary. It is noted that OSHA limits the maximum sulfuric acid concentration in general industry to be 1 mg/m^3 TWA[62]. A wet electrostatic precipitator (wet ESP) was selected as the most appropriate equipment for collecting the sulfuric acid mist. Additionally, this research assumed that the spent soda and wastewater were similarly treated by wastewater treatment. Cost estimations of each treatment are shown below.

1.1 Sulfuric acid-containing gas treatment

As it is previously mentioned that the wet ESP was used to collect the sulfuric acid mist, the economic assessment of wet ESP is shown here. The cost of wet ESP included ESP equipment cost, cost of clean water consumption, and wastewater treatment cost. While the ESP purchased equipment cost was added to the FCI, the cost of clean water and wastewater treatment were included in the operating cost.

For the cost estimation of ESP equipment, according to *EPA Air Pollution Control Cost Manual*, the purchased equipment cost of wet ESP with 95% efficiency is estimated to be \$36.5/in acfm of contaminated gas[21]. The utility information associated with this wet ESP were also obtained from *EPA Air Pollution Control Cost Manual*. The amount of clean water required in this wet ESP is estimated to be 5 gal/min kacfm of contaminated gas. The cost of wastewater treatment from the wet ESP is equal to \$0.002/gallon[21]. The key information and calculation results of the sulfuric acid-containing gas treatment in spent gas and vent gas streams are shown in Table 25.

Table 25 Calculation results of sulfuric acid-containing gas treatment

Items	**Units**	**Spent gas**	**Vent gas**	**Total**
Gas volume	ft3/min	110	6,466	6,576
Equipment cost	MM$/yr	0.004	0.236	0.24
Purchased equipment cost	MM$/yr	0.005	0.278	0.283
Amount of Clean water consumption	MMgal/yr	0.263	15.5	15.7
Cost of wastewater treatment	MM$/yr	$0.527\text{x}10^{-4}$	0.046	0.047

1.2 Wastewater treatment

The cost of wastewater treatment, according to *EPA Air Pollution Control Cost Manual*, is equal to $3.8 per 1000 gal[21]. Using this data, the wastewater treatment costs were determined as shown in Table 26. It should be noted that the amount of wastewater was equal to the amount of clean water consumption.

Table 26 Results of wastewater treatment calculation

Items	**Units**	**Spent soda**	**Wastewater**
Amount of wastewater	MMgal/yr	76.4	37
Cost of wastewater treatment	$/yr	0.29	0.14

2. Total capital investment

Before starting to calculate a total capital investment (TCI), a total purchased equipment cost was carried out by hand-calculation and Activated Economics in Aspen Plus. Most equipment costs were obtained from the Activated Economics in Aspen Plus, except a reactor cost. It was believed that the cost of reactor was higher than the estimated cost from Aspen Plus. Therefore, the costs of reactor in each process were estimated according to the guidelines in *Rules of thumb in engineering practice*[63]. Besides the reactor cost, the costs of additional units including glycerol purification unit, PSA unit, and wet ESP, were calculated by hand. The total purchased equipment cost of wet EPS was acquired from the results in Table 25. The FCI values of glycerol purification unit and PSA unit were determined by applying the ‘Capacity ratio with exponent’ approach to numerical data from Duque, J’s report [58] and HEC, L’s report[64]. All of the economic results should be updated to the present cost by using the cost indices.

The ‘Capacity ratio with exponent’ is defined as [19]:

$$FCI_B = FCI_A(\frac{Capacity_B}{Capacity_A})^x$$

Where FCI_B and FCI_A are the fixed capital investments of plant B and plant A. $Capacity_B$ $Capacity_A$ are the capacities of plant B and plant A. The exponent x was assumed to be 0.6 (sixth-tenths-factor rule).

The ‘cost indices’ is defined as [19]:

$$FOB_{t2} = FOB_{t1}(\frac{Cost\ index\ at\ t1}{Cost\ index\ at\ t2})$$

Where FOB_{t2} and FOB_{t1} are the purchased equipment costs at times t2 and t1, respectively.

According to *Sustainable design through process integration*[19], the fixed capital cost (FCI) is estimated to be five times of the total purchased equipment cost. In addition, this research estimated the working capital (WCI) to be 15% of TCI. Therefore, the value of TCI was calculated by divided FCI by 0.85. The key information and results of TCI calculations for propylene production and isopropanol production are provided in Table 27 and Table 28, respectively.

Table 27 Results of TCI calculation for propylene production

Items	**PDH**	**Glycerol hydro-deoxygenation**
Total purchased equipment cost (MM$/yr)	86.1	44.6
Estimated FCI (MM$/yr)	431	223
FCI of Glycerol purification unit (MM$/yr)	-	165
FCI of PSA unit (MM$/yr)	-	0.107
Total FCI (MM$/yr)	431	388
TCI (MM$/yr)	507	456

Table 28 Results of TCI calculation for isopropanol production

Items	Indirect hydration	Direct hydration	Acetone hydrogenation
Purchased equipment cost (MM$/yr)	26.6	39	13.6
Purchased equipment cost of wet ESP (MM$/yr)	0.388	-	-
Total purchased equipment cost (MM$/yr)	27	195	13.6
Estimated FCI (MM$/yr)	135	195	68
FCI of PSA units (MM$/yr)	-	-	0.002
Total FCI (MM$/yr)	135	195	68
TCI (MM$/yr)	159	229	80

3. Operating cost

A total operating cost is made up of a fixed operating cost and a variable operating cost. The fixed operating cost in this research included salaries and wages, maintenance cost, plant overheads. The fixed operating cost was estimated either from an initial estimation value or as a proportion of FCI. Likewise, the variable operating cost in this research consisted of raw materials cost, utilities cost, and wastewater treatment cost. A detailed calculation of fixed operating costs and variable operating costs is discussed below.

Starting from the details of the fixed operating cost estimation, the labor cost consisted of operating labor cost, supervision and management cost, and direct salary overhead cost. The initial estimation of the operating labor cost was $50,000/shift position/year. A four-shift position was assumed in this calculation. For the other two costs, the supervision and management cost was taken as 25% of the operating labor cost, and the direct salary overhead cost was taken as 50% of the combination of operating labor and supervision costs[20]. With the calculation method mentioned above, the labor cost was estimated to be $375,000/year. While it was simple to calculate the maintenance cost (The maintenance cost was equal to 5% of FCI)[19], it was more complicated to calculate corporate overhead charges. The corporative overhead charges included the research and development (R&D) cost, selling and marketing cost, and general and administrative (G&A) cost. These costs could be estimated as a proportion of revenues and operating labor cost according to *Chemical engineering design*[20], as described in Table 29. It should be noted that the selling and marketing cost highly depended on types of product. The selling and marketing cost was approaching zero for ASTM standard commodities[20]. Thus, the selling and marketing cost was assumed to be zero in this calculation. A summary of calculation methods to determine the fixed operating cost is listed in Table 29. Moreover, the results of the fixed operating cost of processes for propylene production and isopropanol production in this research is shown in Table 30 and Table 31.

Table 29 Calculation methods for estimating fixed operating cost

Items	Methods
Operating labor cost	Approximated to be $200,000/shift/year
Labor cost	$0.625xOperating\ labor\ cost$
Maintenance cost	$0.05xFCI$
R&D cost	$0.01xRevenues$
G&A cost	$0.65xLabor\ cost$
Selling and Marketing cost	0
Corporative overhead charges	$R\&D\ cost + G\&A\ cost + Selling\ and\ Marketing\ cost$
Fixed operating cost	$Labor\ cost + Maintenance\ cost + Corporative\ overhead\ charge$

Table 30 Results of fixed operating cost estimation for propylene production

Items	PDH	Glycerol hydro-deoxygenation
Labor cost (MM$/yr)	0.375	0.375
Maintenance cost (MM$/yr)	21.5	19.4
R&D cost (MM$/yr)	3.62	3.49
G&A cost (MM$/yr)	0.244	0.244
Comparative overhead charges (MM$/yr)	3.87	3.73
Fixed operating cost (MM$/yr)	25.8	25.1

Table 31 Results of fixed operating cost estimation for isopropanol production

Items	**Indirect hydration**	**Direct hydration**	**Acetone hydrogenation**
Labor cost (MM$/yr)	0.375	0.375	0.375
Maintenance cost (MM$/yr)	6.75	9.74	3.4
R&D cost (MM$/yr)	4.97	4.31	4.44
G&A cost (MM$/yr)	0.244	0.244	0.244
Comparative overhead charges (MM$/yr)	5.21	4.56	4.69
Fixed operating cost (MM$/yr)	13.2	14.7	9.16

For the variable operating cost calculation, it was a simple calculation. The cost of raw materials was determined by adding costs of raw material in the process. The cost of raw material was carried out by multiplying the chemical price to its input in the process. The input data was obtained from the process simulation result. Similarly, the cost of utilities was calculated by adding the multiplications of the price of utility and the amount of utility used in the process. It should be noted that the prices of utilities in this research are given in Appendix B. The wastewater treatment was obtained from Table 26. Additionally, the utilities cost for glycerol purification was estimated from Duque, J[58]. The calculation results of the total operating cost of each process in this research are presented in Table 32 and Table 33.

Table 32 Calculation results of total operating cost for propylene production

Items	PDH	Glycerol hydro-deoxygenation
Raw materials cost (MM$/yr)	163	84.1
Utilities cost (MM$/yr)	45.4	271
Wastewater treatment cost (MM$/yr)	-	-
Variable operating cost (MM$/yr)	209	355
Fixed operating cost (MM$/yr)	25.8	25.1
Total operating cost (MM$/yr)	234	380

Table 33 Calculation results of total operating cost for isopropanol production

Items	Indirect hydration	Direct hydration	Acetone hydrogenation
Raw materials cost (MM$/yr)	400	332	429
Utilities cost (MM$/yr)	8.45	16.8	0.608
Wastewater treatment cost (MM$/yr)	0.478	-	-
Variable operating cost (MM$/yr)	409	349	430
Fixed operating cost (MM$/yr)	13.2	14.7	9.16
Total operating cost (MM$/yr)	422	364	439