Simulation of Polymeric Precursors Production from Wine Industrial Organic Wastes

Tanapoom Phuncharoen, Tawiwat Sriwongsa, Kanita Boonruang, Apichit Svang-ariyaskul

Abstract—The production of Dimethyl acetal, Isovaleradehyde and Pyridine were simulated using Aspen Plus simulation. Upgrading cleaning water from wine industrial production is the main objective of the project. The winery waste composes of Acetaldehyde, Methanol, Ethyl Acetate, 1-propanol, water, *iso*-amyl alcohol and *iso*-butyl alcohol. The project is separated into three parts; separation, reaction, and purification. Various processes were considered to maximize the profit along with obtaining high purity and recovery of each component with optimum heat duty. The results show a significant value of the product with purity more than 75% and recovery over 98%.

Keyword—Dimethyl acetal, Pyridine, wine, Aspen Plus, Isovaleradehyde, polymeric precursors.

I. INTRODUCTION

WINERY business has been growing nowadays. The processes related to winery business especially cleaning process are interested by winery business investor for the turnover. Wines contain many chemical compounds identical to those in fruits, vegetables, and spices. The waste composed of Acetaldehyde, Ethyl acetate, *n*-Propanol, *iso*-butyl alcohol, *iso*-amyl alcohol, and Methanol as shown in Table I. This project aims to upgrade of winery waste in order to save the environment and increase the key product value. This project can help to develop the wine industrial. There are three main reactions that will be used to upgrade the value of the waste: (1) The production of Dimethyl acetal from acetaldehyde and methanol, (2) The production of pyridine from acetaldehyde, and (3) The production of Isovaleradehyde from *iso*-amyl alcohol. For this project the separation process is to be done first using separation units such as distillation column, flash drums, and extraction. After the separation, chemical reactions of selected components are to be done next and end up with purification process.

Dimethyl acetal and Isovaleradehyde are promising products that can be produced and use as polymeric precursors while use pyridine as a solvent in polymer process.

Polymer is an everyday use materials such as paper, plastic, bottle, etc. The demand for polymer is very high due to it has many uses and applications. Making monomer as a precursor to polymer is possible due to industrial process of creating monomer or polymer is available. Initial reactants from cleaning can be used to create monomer that can be sold for adequate price.

Tanapoom Phuncharoen, Tawiwat Sriwongsa, and Kanita Boonruang were with the School of Bio-Chemical Engineering and Technology, Sirindhorn International Institute of Technology, Thammasat University, 99 Phaholyothin Road, Pathum Thani, Thailand 12121 (e-mail: tanapoom.phuncharoen@gmail.com, tawiwat.s@gmail.com, kanita.boonruang@gmail.com).

Apichit Svang-Ariyaskul is with School of Bio-Chemical Engineering and Technology, Sirindhorn International Institute of Technology, Thammasat University, 99 Phaholyothin Road, Pathum Thani, Thailand 12121 (corresponding author to provide phone: 662-986- 9103, fax: 662-986-9112; e-mail: apichit@siit.tu.ac.th).

TABLE I
COMPONENT AND COMPOSITION OF ORGANIC WASTE WATER IN WINE INDUSTRY

Component	Mass flow rate (kg/hr)
Acetaldehyde	5.40
Methanol	7.40
Ethyl Acetate	8.96
1-propanol	0.98
Water	53.27
iso-butyl alcohol	2.93
iso-amyl alcohol	12.70

The objective of this project is to separate the mixture of waste and undergoes chemical reactions to increase the value of the waste. Products after reacted should be within the same theme of production. The mixture consists of Acetaldehyde, Ethyl Acetate, 1-propanol, *iso*-butyl alcohol, *iso*-amyl alcohol, and Methanol. The design aims to maximize the profit along with high purity and recovery of each component and also minimize operating cost as much as possible.

II. PROCESS DESIGN

Feed consists of water, Acetaldehyde, Ethyl Acetate, *1*-propanol, *iso*-butyl alcohol, *iso*-amyl alcohol, and Methanol is to be separated before reaction process.

Feed firstly enter the Extraction unit-1 to separate Methanol and water to the top stream and Acetaldehyde, Ethyl Acetate, 1-propanol, *iso*-butyl alcohol, *iso*-amyl alcohol, and n-pentane to the bottom stream using n-Pentane as a solvent. Mixture of Methanol and water is separated using Distillation column 1 to obtain high purity of Methanol for Dimethyl acetal production. Mixture of Acetaldehyde, Ethyl Acetate, 1-propanol, *iso*-butyl alcohol, *iso*-amyl alcohol, and n-pentane is separated using Distillation column 2. Distillate stream consists of Acetaldehyde, Methanol, and n-pentane while bottom stream consists of Ethyl Acetate, 1-propanol, *iso*-butyl alcohol, and *iso*-amyl alcohol. Flash drum-1 is constructed to separate the distillate stream with KVL as a separation factor. By using Flash drum-1, n-Pentane will vaporize while Acetaldehyde and Methanol stays in liquid form and leave at the bottom of the unit.

Absorption unit-1 is constructed to separate the Bottom stream consisting of Ethyl Acetate, 1-propanol, *iso*-butyl

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:7, No:12, 2013

alcohol, and *iso*-amyl alcohol. Bottom stream is heated to become vapor and flow up along the absorption unit along and contact with Ethylene Glycol that is fed from the top in liquid phase. As a result, Ethyl Acetate leaves to the top stream in vapor while *iso*-butyl alcohol, 1-propanol, *iso*-amyl alcohol, and Ethylene Glycol leave to the bottom stream in liquid phase. The bottom stream from the first absorption unit is heated to become vapor and pass through Absorption unit-2 contacting with Acetone that is fed from the top in liquid phase. Ethylene Glycol which does not dissolve in Acetone leaves to the bottom stream and *iso*-amyl alcohol along with Acetone leaves to the top stream. After the Absorption unit-2, mixture of Acetone, *iso*-amyl alcohol, and *iso*-butyl alcohol is to be separated using extractive distillation column with Acetone acting as a solvent. The distillation column separated Acetone and *iso*-butyl alcohol as a distillate stream and high purity, *iso*-amyl alcohol as a bottom stream.

In the reaction process, Ethyl Acetate and water is used to produce Ethanol and Acetic acid using Plug Flow reactor-1. Ethanol is a precursor material to produce Acetaldehyde. Oxygen is fed to react with Ethanol to produce Acetaldehyde in Plug Flow reactor-2. Before further production of Dimethyl

acetal and Pyridine, Acetaldehyde needs to be separated from Acetic acid and water. Distillation column-3 is used to separate the mixture. Acetaldehyde after separation goes through splitter to separate into two streams for Dimethyl acetal and Pyridine production. Most of Acetaldehyde is fed to produce Dimethyl acetal while the excess Acetaldehyde is used to produce Pyridine. Dimethyl acetal is produced by Methanol reacts with Acetaldehyde with water as by-product using Plug Flow reactor-3.

Excess Acetaldehyde is used to react with Formaldehyde and Ammonia to make Pyridine with water and Hydrogen as by-product using Plug flow reactor-4. Isovaleraldehyde is produced by dehydration reaction of *iso*-amyl alcohol with hydrogen as by-product using Plug flow reactor-5.

Purification is the next process to obtain high purity of each product. Distillation column-5 is used to separate a mixture of Dimethyl acetal from water. Extractive Distillation column-6 is used to separate to separate a mixture of Pyridine and water using Sulfolane as a solvent. Distillation column-7 is used to separate a mixture of Pyridine and Sulfolane. Flash drum-2 is used to separate a mixture of Isovaleraldehyde and Hydrogen.
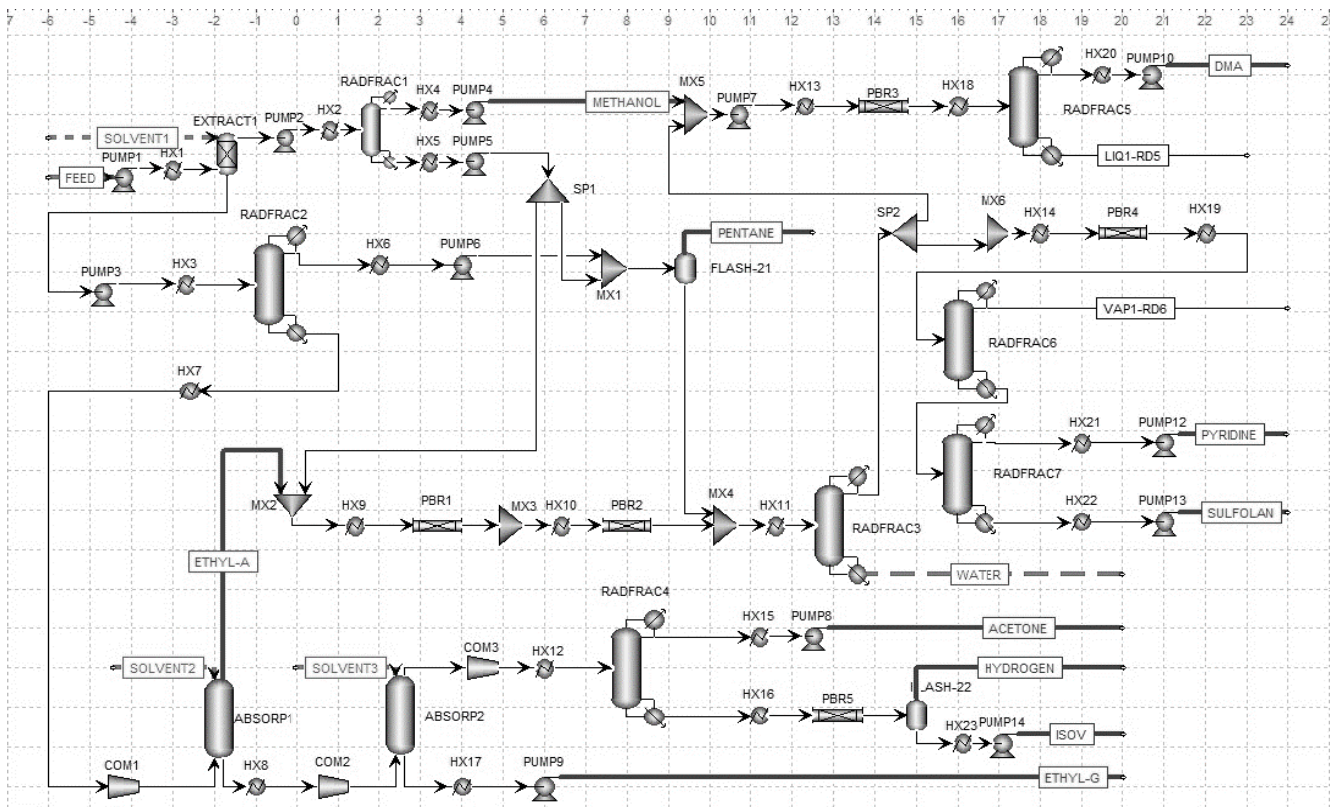

Fig. 1 Schematic diagram for Process Simulation to Polymeric Precursors from Wine Industrial Organic Waste

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:7, No:12, 2013

TABLE II
REACTION AND RATE EXPRESSION OCCURRING IN PROCESS

No.	Reaction	Rate expression
1	$2\,CH_3OH + CH_3CHO \rightarrow CH_3CH(OCH_3)_2 + H_2O$	$-r_{DMA} = k_c(a_{CH_3OH}\,a_{CH_3COH} - \dfrac{a_{CH_3CH(OCH_3)_2}\,a_{H_2O}}{K_{eq}\,a_{CH_3OH}})$
2	$2\,CH_3CHO + HCHO + NH_3 \rightarrow C_5H_5N + 3\,H2O + H_2$	$-r_{Pyridine} = (k_1 - k_2)C_A^2\,a$
3	$C_5H_{12}O \rightarrow (CH_3)_2CHCH_2CHO + H_2$	$-r_{Isovaleraldehyde} = \dfrac{k[(P_A - (\frac{P_I P_H}{K_e}))]}{(1 + K_I P_I)}$
4	$CH_3CH_2OH + \frac{1}{2}O_2 \rightarrow CH_3CHO + H_2O$	$-r_{Acetaldehyde} = \dfrac{k_1 P_1}{(1 + \dfrac{k_1 P_1}{k_{ox} P_{O_2}^{1/2}})}$
5	$CH_3COOCH_2CH_3 + H_2O \rightarrow CH_3CH_2OH + CH_3COOH$	$-r_{Ethanol} = kC_A$

No.1: Dimethyl acetal synthesis, No.2: Pyridine synthesis, No.3: Isovaleraldehyde synthesis, No.4: Acetaldehyde production, No.5: Ethanol production (Ethyl acetate hydrolysis)

TABLE III
REACTION AND RATE CONSTANT IN PROCESS

Reaction number	Kinetic			Equilibrium		
	variable	k_0 (gmol/gcat·min)	Ea (J/gmol)	variable	ΔH (J/gmol)	ΔS (J/gmol·K)
1	k_c	759000000.000	48670.000	K_{eq}	-17487.81	-33.7322
2	k_1	155086.850	23848.800	-	-	-
	k_2	79988.773	25689.760	-	-	-
3	k	484380.000	42.392	K_{eq}	65000	116.1074
				K_1	34.162	-51.2655
4	k_1	299539.028	45605.90	-	-	-
	k_{ox}	35242.217	48952.800	-	-	-
5	k	5247000.000	41140.000	-	-	-

No.1: Dimethyl acetal synthesis, No.2: Pyridine synthesis, No.3: Isovaleraldehyde synthesis, No.4: Acetaldehyde production, No.5: Ethanol production (Ethyl acetate hydrolysis)

III. REACTION PROCESS

Total of five reactions were done to upgrade wine industrial organic waste to three polymeric precursors. Polymeric precursors that are produced are Dimethyl acetal, Pyridine, and Isovaleradehyde. Orders of reactions are based on scheme created using Aspen Plus simulation.

Moreover, Van't Hoff equation is used to determine equilibrium constant. Van't Hoff equation relates the change in the equilibrium constant K of a reaction to the change in temperature. It is derived from Gibbs equation which gives the temperature dependence of the Gibbs free energy.

$$\ln K_{eq} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (1)$$

$K_{eq} = Equilibrium\ constant\ of\ a\ chemical\ reaction$
$\Delta H^0 = Enthalpy\ change\ of\ a\ chemical\ reaction$
$\Delta S^0 = Entropy\ change\ of\ a\ chemical\ reaction$
$R = Gas\ constant$ ($8.314462\ J/mol \cdot K$)

Arrhenius Equation use to represent the effect of a change of temperature on the rate constant because this equation show the relationship between the rate a reaction and its temperature also include activation energy. From the Arrhenius equation can be expressed as

$$k = k_0 exp^{(\frac{-Ea}{RT})} \qquad (2)$$

$k_0 = rate\ constant\ of\ a\ chemical\ reaction$
$Ea = activation\ energy$

$R = Gas\ constant$ ($8.314462\ J/mol \cdot K$)

A. Conversion of Ethyl Acetate and Water to Ethanol

Ethanol can be produced through hydrolysis reaction of Ethyl Acetate. Ethanol plays an important role to maximize the profit by later convert to Acetaldehyde which will be used to produce Dimethyl acetal. The catalyst that is used to undergo the reaction is support enzyme in aqueous phase. The reaction occurs at 45°C with operating pressure between 1-3 bars. The conversion of Ethyl Acetate is 40-50% [1]. Similar process with different catalyst was studied. The catalyst that is used to undergo the reaction is acidic cation exchange resin or Amberlyst-15. The reaction occurs between 40-70°C with operating pressure at 1 atm. The conversion of Ethyl Acetate ranges from 60-80% with high contact time and require excess feed of water [2].

B. Conversion of Ethanol and Oxygen to Acetaldehyde

Ethanol can be converted to Acetaldehyde to maximize the amount of Acetaldehyde to use for Dimethyl acetal that gives the highest profit. It can be converted through Oxidative Dehydrogenation reaction. The catalyst that is used to undergo the reaction is grafting vanadyl triisopropoxide onto a silica support whose surface was coated with TiO_2 (V_2O_5/TiO_2-SiO_2). The reaction occurs between 150 to 250°C with operating pressure at 1 atm. At 180°C, the conversion of Ethanol is 80-90% along with high selectivity of Acetaldehyde above 80% [3]. Similar process with different catalyst was studied. The catalyst that is used to undergo the reaction is Sodium-promoted vanadium oxide catalysts support on MCM-

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:7, No:12, 2013

41 and TiO$_2$. The reaction occurs between 127 to 427°C with operating pressure at 1 atm. The conversion of ethanol is between 10-20% with selectivity of Acetaldehyde above 80% [4].

C. Conversion of Acetaldehyde and Methanol to Dimethyl acetal

Acetaldehyde produced from Ethanol is separated to two streams, one for Dimethyl acetal production and another stream for Pyridine production. Dimethyl acetal can be produced through synthesis reaction of Methanol and Acetaldehyde. The catalyst that is used to undergo the reaction is smopex-101 fiber catalyst. The reaction occurs between 10 to 40°C and the operating pressure of the process is 0.6 MPa. The conversion of Acetaldehyde is 60-70% [5]. Similar process with different catalyst was studied. The catalyst that is used to undergo the reaction is acid resin Amberlyst-15 catalyst. The reaction occurs between 20 to 60°C with operating pressure at 1 MPa. The conversion of Acetaldehyde is 60-70% [6].

D. Conversion of Acetaldehyde with Formaldehyde and Ammonia to Pyridine

Acetaldehyde can be converted to Pyridine through aminocylisation reaction in vapor phase that requires Acetaldehyde to react with formaldehyde and ammonia to produce Pyridine. The catalyst that is used to undergo the reaction is deactivating HZSM-5 catalyst. The reaction occurs between 200 to 280°C and the operating pressure of the process is 1 atm. The conversion of Acetaldehyde is 70-80% [7].

E. Conversion of Iso-Amyl Alcohol to Isovaleraldehyde

Iso-amyl alcohol can be converted to Isovaleraldehyde through dehydration reaction. The catalyst that is used to undergo the reaction is a series of zinc-promoted copper catalyst. The reaction occurs between 230 to 290°C and operating pressure is 1 atm. The conversion of iso-amyl alcohol is 60-80% [8].

IV. SEPARATION PROCESS

The main component that needed to be considered as raw materials was Methanol, Acetaldehyde, Ethyl acetate and iso-amyl alcohol. However, water needed to separate first due to azeotrope formation. N-Pentane is used as solvent in order to extract ester, aldehyde and short-chain alcohol (C$_2$-C$_5$), i.e. iso-butanol, iso-amyl alcohol, where raffinate remains only methanol and water. Addition, N-Pentane is generally used as wine aroma extraction solvent due to high extracting capability [9], [10]. Whereas, Methanol and water could be separated easily because Methanol have high relative volatility compare with water. Addition, ethyl acetate hydrolysis and ethanol oxidation reaction are conducted in order to increase feedstock for Dimethyl acetal (DMA) production [2]. Acetaldehyde was simply separate in RADFRAC3 because of high relative volatility as well. The complexity of separation process take placed from Ethyl acetate separation because of hydrogen bound formation between ester and short-chain alcohol. Hence, absorption column is utilized with Ethylene glycol as solvent due to the fact that Ethylene glycol is highly miscible in alcohol but not dissolve in ester i.e. Ethyl acetate [11]. Moreover, absorption column not required energy for separation which reduce overall utility cost. Similar to Ethyl acetate separation, iso-Amyl alcohol was distinguished from iso-Butanol via extractive distillation column by addition of acetone. Acetone is generally used as solvent to promote relative volatilities of alcohol.

V. PURIFICATION PROCESS

The simplest purification is DMA and its by-product, water, because DMA have enormous different boiling point from water. Similar to DMA purification, Isovaleraldehyde could be easily purified because of iso-amyl alcohol feedstock have high purity. By-product of Isovaleraldehyde production is hydrogen which can further utilize as on-site fuel for electricity generation. However, the remaining Acetaldehyde is value-added by using as raw material for Pyridine production because of pyridine widely use as polymeric precursor to produce 2-Vinlypyridine. Addition, 2-Vinlypyridine is used in latex terpolymer synthesis for an application as tire-cord binder [12]. Pyridine production process has high difficulty in purification due to Pyridine and its by-product, water, have azeotrope formation and strong intermolecular interaction, so normal distillation is not appropriate with pyridine purification. Therefore, extractive distillation column is used. Sulfolane is selected as a solvent due to several reasons: (1) Sulfolane has high boiling point which easily to recover (2) Sulfolane is mainly available use as extraction solvent in many chemical plant (3) Sulfolane is relatively inexpensive compare to alternative solvent e.g. Isophorone [13].

VI. RESULT AND DISCUSSION

Aspen Plus was used to simulate and to design the process. The thermodynamic model was UNIQUAC. All distillation towers were RADFRAC model. The results and discussions were conducted via unit operations and overall process. The basis of the work had feed volume of 2,400 l/day which consists of Acetaldehyde, Methanol, Ethyl acetate, 1-Propanol, water, iso-butanol and iso-amyl alcohol.

A. Methanol Separation (EXTRACT1)

Methanol separation was conducted by using normal extraction process where n-Pentane was used as extractive solvent. N-pentane is used because of high extracting capability and widely use in wine aroma extraction process [9], [10]. EXTRACT1 was optimized so that Methanol recovery and purity were over 99% while the solvent utilization was minimized. In addition, an appropriate mass flow rate of n-pentane is 70 kg/hr because the recovery of Methanol is high where operating condition is 25°C, 1 atm. A suitable solvent amount effect directly to the number of stage in extraction unit where optimized condition only 5 trays are required. However, Methanol purity is relatively low due to water contamination which further purified in RADFRAC1.

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:7, No:12, 2013

B. Methanol Purification (RADFRAC1)

Methanol purification was carried through normal distillation, since Methanol and water have huge different in relative volatilities. Addition, Methanol's boiling point is 64.7°C while water's boiling point is 100°C. RADFRAC1 was optimized in order to provide the highest purity and recovery of Methanol, whereas the energy consumption was minimized by alternating the reflux ratio, number of stage, feed stage, and feed temperature. The optimal design column had 20 stages, feed stage of 5, condenser pressure and temperature of 1 atm and 67.55°C, re-boiler pressure and temperature of 1.5 atm and 111.8°C, reflux ratio of 0.8, and distillate to feed ratio of 0.1.

C. Acetaldehyde Separation (RADFRAC2) and n-Pentane Recovery (FLASH-21)

Acetaldehyde separation was conducted via normal distillation because the mixture in inlet is unlikely to be separated by liquid-liquid extraction due to sharing similar miscibility properties. Moreover, azeotrope is not available result in feasibility of separation process. Since there are many components, KVL value is used in order to justify where to cut the mixture into two streams. The optimum design conditions are 11 stages, feed stage of 4, condenser pressure and temperature of 1 atm and 32.31°C, re-boiler pressure and temperature of 1.5 atm and 110.37°C where the reflux ratio of 0.44, and distillate to feed ratio of 0.8. Addition, decreasing reflux ratio leads to impurity of Acetaldehyde in the distillate stream, whereas decreasing distillate to feed ratio reduce mass flow rate and recovery of Acetaldehyde in distillate stream. However, distillate stream is containing tertiary mixture consists of Acetaldehyde, water and n-Pentane. Hence, solvent recovery is further conducted.

N-pentane is recovered from the mixture by utilize understanding in Thermodynamic properties. According to the fact, n-Pentane has the highest relative volatilities, thus n-Pentane tend to vaporize naturally. Therefore, FLASH-21 is pressurized to increase internal energy of n-Pentane which results in reducing heat of vaporization follow the first law of Thermodynamic. Therefore, n-Pentane is completely vaporized with minimum heat duty requirement where 99% recovery and 99% purity were obtained. The optimum operating conditions are 25°C and 10 atm.

D. Ethyl Acetate Separation (ABSORP1)

Ethyl acetate was separated from short-chain alcohol by utilize absorption column where Ethylene Glycol is used as a solvent. Ethylene Glycol has high affinity with alcohol, but low affinity with ester. Therefore, Ethylene glycol is able to strip short-chain alcohol, i.e. iso-butanol, iso-amyl alcohol, downward where Ethyl acetate was vaporized upward without dissolving in Ethylene Glycol. The optimal operating conditions are 191.85°C of inlet temperature and 0.6 atm of pressure drop along the column and 22.5 kg/hr Ethylene Glycol mass flow rates. Addition, increasing pressure drop results in reducing of Ethyl Acetate recovery where increasing solvent mass flow rates are decrease Ethyl acetate recovery as well.

E. Ethylene Glycol Recovery (ABSORP2)

Ethylene recovery was done by using absorption column. Solvent utilize is Acetone because of high affinity with alcohol, but low affinity to diols group. The optimum condition is obtained at Acetone mass flow rates equal to 44 kg/hr and temperature of 266.85°C. Moreover, two main parameters were considered which are inlet temperature and solvent, Acetone, mass flow rate. Lowering temperature effected in decreasing of iso-amyl alcohol recovery where insufficient solvent resulted in decreasing iso-amyl alcohol recovery as well.

F. Ethyl Acetate Hydrolysis (PBR1)

Ethyl acetate was feed into PBR1, Plug-flow reactor, in order to produce Ethanol via ester hydrolysis reaction. Ethanol was used as a precursor to produce acetaldehyde. Ethyl acetate hydrolysis is utilized Amberlyst-15 catalyst with bed void of 0.445 and particle density equal to 1080 kg/m^3. The optimized condition occurs at isothermal condition where temperature of reactor equal to 91.85°C and length of reactor equal to 1.3 meter because of Acetic acid and Ethanol are produced the most. Addition, Hydrolysis reaction is exothermic reaction where the heat is released, so isothermal condition is selected in order to maintain reactor temperature at certain point. As a result, reaction was driven forward relatively fast compare to adiabatic condition which reduce overall reactor length.

G. Acetaldehyde Production (PBR2)

PBR2 is used to produce Acetaldehyde in order to increase feedstock for DMA production. The simulation was performed with V_2O_5/TiO_2-SiO_2 catalyst where operating temperature range is 99.85-179.85°C, 0.445 void fraction and particle density equal to 3300 kg/m^3. Optimized condition is obtained at 79.85°C and overall reactor length is 0.5 meter due to reaction reach maximum conversion. Moreover, Acetaldehyde production is also exothermic reaction, hence isothermal condition is selected to maintain reactor temperature.

H. Acetaldehyde Purification (RADFREAC3)

Acetaldehyde purification is conducted via normal distillation because Acetaldehyde has high relative volatilities compare to water and acetic acid. Acetaldehyde purity is required to produce Dimethyl acetal and Pyridine without contamination. RADFRAC3 was optimized in order to provide the highest purity and recovery of Acetaldehyde, whereas the energy consumption was minimized by alternating the reflux ratio, number of stage, feed stage, and feed temperature. The optimal design column had 20 stages, feed stage of 4, condenser pressure and temperature of 1 atm and -70.948°C, re-boiler pressure and temperature of 1.5 atm and 112.325°C, reflux ratio of 0.1, and distillate to feed ratio of 0.1.

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:7, No:12, 2013

I. Iso-Amyl Alcohol Purification (RADFRAC4)

According to the fact, *iso*-butanol and *iso*-amyl alcohol have several similarities either physical properties or Thermodynamic properties. Therefore, *iso*-amyl alcohol could not purify through normal distillation column. Extractive distillation with Acetone as a solvent was applied. Acetone is used to promote relative volatilities of *iso*-butanol. Addition, *iso*-butanol and *iso*-amyl alcohol have slightly different relative volatilities. Hence, a number of stage requirements were decrease and separation process is feasible. The optimal design column had 20 stages, feed stage of 2, condenser pressure and temperature of 1 atm and 62.57°C, re-boiler pressure and temperature of 1.5 atm and 144.78°C, reflux ratio of 0.1, and distillate to feed ratio of 0.9.

J. Dimethyl Acetal (DMA) Production (PBR3)

PBR3 unit is used to produce Dimethyl acetal with smopex-101 fiber catalyst. Addition, smopex-101 fiber catalyst has bed void of 0.267 and particle density equal to 567 kg/m^3. Dimethyl acetal (DMA) can be produced through synthesis reaction of Methanol and Acetaldehyde. The reaction occurs between 10 to 40 °C and the operating pressure of the process is 0.6 MPa. The conversion of Acetaldehyde is 60-70% [C]. The optimum design condition is 1 meter reactor length and 31.85°C operating temperature.
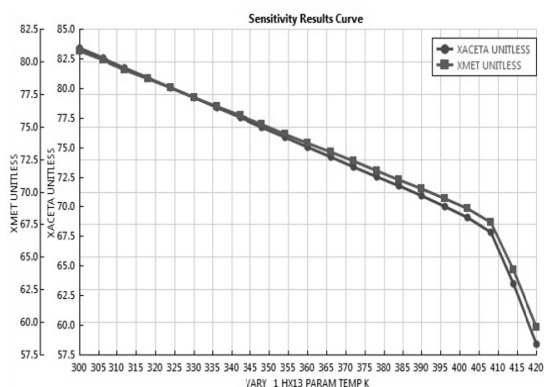

Fig. 2 Effect of temperature on Acetaldehyde and Methanol conversion
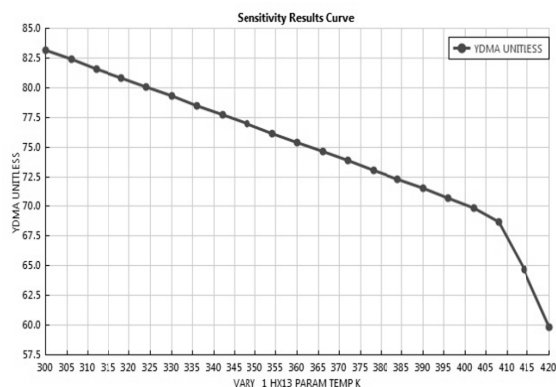

Fig. 3 Effect of temperature on Dimethyl acetal yield

K. Pyridine Production (PBR4)

Excess Acetaldehyde from Dimethyl acetal is used to produce Pyridine. Pyridine is an important polymeric precursor to 2-vinlypyridine that is use to produce latex. Pyridine is produced by synthesis reaction of Acetaldehyde, Formaldehyde, and Ammonia to give Pyridine, Hydrogen, and water. The reaction occurs at 473-533 K and operating pressure at 1 atm. The conversion of Acetaldehyde is 70-80%. The catalyst uses in the reaction is deactivating HZSM-5 catalyst with 5kg loading, bed void equal to 0.445, and particle density is 3.1847 kg/m^3. Increasing loading of catalyst over the reference results in higher conversion [7].

L. Dimethyl Acetal (DMA) Purification (RADFRAC5)

Separation of Dimethyl acetal and water into separated stream is required to achieve high purity of Dimethyl acetal. However, Dimethyl acetal and water forms strong interaction between each other that leads to the narrow T-xy diagram. Narrow T-xy diagram indicates high number of stages of distillation column required to separate the mixture. With maximum of fixed number of stage of distillation at 20 stages, distillate to feed and reflux ratio are factors that affect separation process. At distillate to feed ratio equals to 0.5 and reflux ratio equals to 0.4, it is the optimum condition that Dimethyl acetal has high purity with moderate heat duty required. Purity of Dimethyl acetal is 77.41%.

M. Pyridine Purification and Sulfolane Recovery (RADFRAC6 & RADFRAC7)

After the synthesis reaction process of Pyridine, Pyridine, water and Hydrogen are obtained. Pyridine is an important polymeric precursor to 2-vinlypyridine that is use to produce latex. Separation process is required to get high purity of Pyridine. However, Pyridine is highly soluble in water and water forms azeotrope. Not only T-xy is narrow, purity is limited if distillation column is used since azeotrope is formed. Extractive distillation column is used to separate the mixture. Extractive distillation is the use of solvent to enhance the separation process. Sulfolane is used as a solvent for Extractive distillation. Due to the similarity in structure of Sulfolane and Pyridine, Pyridine will be soluble in Sulfolane instead of water and allowed water to be separated out. Optimum condition is distillate to feed ratio equal to 0.4 and reflux ratio is equal to 0.1 with moderate heat required. Water vaporized to the top while Pyridine and Sulfolane leaves at the bottom. Further separation of Pyridine and Sulfolane is required.

Pyridine and Sulfolane can be easily separated using a distillation column due to the wide T-xy diagram of the binary system. Parameters to be adjusted are distillate to feed ratio and reflux ratio. At optimum condition operated, purity of Sulfolane is 99.96% with recovery of 99.03% and purity of Pyridine is 87.84%.

N. Isovaleraldehyde Production (PBR5)

Isovaleraldehyde is produced through dehydration reaction of *iso*-amyl alcohol. The purpose of this reaction is to add

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:7, No:12, 2013

value to the large amount of *iso*-amyl alcohol. The reaction yields Hydrogen as by-product which is valuable. The catalyst that is used is Zinc-promoted copper catalyst that yields a conversion of *iso*-amyl alcohol around 60-80%. The temperature ranges from 230-290°C with operating pressure at 1 atm [8].

O. Fuel Gas Separation (FLASH-22)

A mixture of Isovaleraldehyde and hydrogen is obtained from dehydration of *iso*-amyl alcohol. Separation process is required to obtain high purity of Isovaleraldehyde. The separation of this mixture is not complicated since at room temperature, hydrogen is in gas phase (boiling point = -252.879°C) and Isovaleraldehyde is in liquid phase (boiling point = 90°C). Flash drum is used to separate mixture of two phases to obtain high purity of Isovaleraldehyde. Purity of Isovaleraldehyde is 96.46%.

TABLE IV
CATALYST SELECTION CONDITION SUMMARY

	PBR3	PBR4	PBR5
Catalyst	Smopex 101 fiber	Deactivating HZSM-5	Zinc-promoted copper
Temp Variation	260-380 K	330-400 K	350-390 K
Reactor Length Variation	0.5-2 meter	0.5-2 meter	0.5-2 meter
Optimum Temp	305 K	330 K	350 K
Optimum Length	1 meter	1 meter	1 meter
Result	9.31 kg/hr	3.07 kg/hr	7.66 kg/hr

TABLE V
RECOVERY AND PURITY SUMMARY

	Compounds	Recovery	Purity
SOLVENT	n-pentane	99.57	98.76
	Ethylene Glycol	98.31	89.50
	Acetone	100	86.88
	Sulfolane	99.04	99.97
	DMA	100	77.41
PRODUCT	Pyridine	98.61	87.85
	Isovaleraldehyde	98.47	96.49
	Hydrogen	99.98	60.54

VII. CONCLUSION

Process design to produce polymeric precursors from organic waste water in wine industrial production was simulated using Aspen Plus simulation. The main objective is to convert Methanol, Ethyl Acetate, 1-propanol, water, *iso*-amyl alcohol and *iso*-butanol to higher value components. Methanol and Acetaldehyde is converted to Dimethyl acetal. Excess Acetaldehyde is converted to Pyridine. *Iso*-amyl alcohol is converted to Isovaleraldehyde. The proposed process is to maximize the purity of Dimethyl acetal along with minimum heat duty. This process aims to develop a process to utilize the waste water into valuable products instead of direct disposal of the wastewater.

NOMENCLATURE

r_{DMA}	rate of reaction(mol/kg·s)
K_{eq}	Equilibrium reaction constant ($\frac{m^3}{mol}$)
k_c	Kinetic constant (mol/g min)
a	Liquid-phase activity
k_1	Reaction rate constant of Pyridine formation ($\frac{lt^2}{g.cat.h.mol}$)
k_2	Reaction rate constant of 3-Picolines formation ($\frac{lt^2}{g.cat.h.mol}$)
C_A	Concentration of A in bulk fluid (g/mol/cm^3)
$r_{Pyridine}$	Rate of reaction,(gmole/gcat-h)
k	Reaction rate constant of isoamylalcohol (gmole/gcat-h atm)
P_A	Partial pressure of isoamylalcohol (atm)
P_I	Partial pressure of isovaleraldehyde (atm)
P_H	Partial pressure of hydrogen(atm)
K_I	Adsorption constant of isovaleraldehyde (atm)
K_e	Equilibrium constant of dehydrogenation of isoamyl alcohol (atm)
X_A	Conversion of dehydrogenation of isoamyl alcohol
$-r_{Acetaldehyde}$	Rate of reaction
P_{O_2}	Partial pressure of Oxygen (atm)
P_1	Partial pressure of ethanol in the gas mixture (atm)
k_{ox}	Kinetic constant for catalytic site reoxidation
Ea	activation energy(kcal/mol)
A	preexponential factor for kinetic constant
$r_{Ethanol}$	Rate of reaction
k	Reaction rate constant of ethanol
C_A	Concentration of A in bulk fluid

REFERENCES

[1] Perez, V. H.; Miranda, E. A.; Valença, G. P., Kinetics of gas-phase hydrolysis of ethyl acetate catalyzed by immobilized lipase. *Applied biochemistry and biotechnology* 2007, *136* (1), 23-37.

[2] Ayyappan, K.; Toor, A. P.; Gupta, R.; Bansal, A.; Wanchoo, K., Catalytic Hydrolysis of Ethyl Acetate using Cation Exchange Resin (Amberlyst-15): A Kinetic Study. *Bulletin of Chemical Reaction Engineering & Catalysis* 2010, *4* (1), 16-22.

[3] Tesser, R.; Maradei, V.; Di Serio, M.; Santacesaria, E., Kinetics of the oxidative dehydrogenation of ethanol to acetaldehyde on V2O5/TiO2-SiO2 catalysts prepared by grafting. *Industrial & engineering chemistry research* 2004, *43* (7), 1623-1633.

[4] Chimentao, R. J.; Herrera, J. E.; Kwak, J. H.; Medina, F.; Wang, Y.; Peden, C. H., Oxidation of ethanol to acetaldehyde over Na-promoted vanadium oxide catalysts. *Applied Catalysis A: General* 2007, *332* (2), 263-272.

[5] Gandi, G. K.; Silva, V. M.; Rodrigues, A. E., Acetaldehyde dimethylacetal synthesis with Smopex 101 fibres as catalyst/adsorbent. *Chemical engineering science* 2007, *62* (4), 907-918.

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:7, No:12, 2013

[6] Gandi, G. K.; Silva, V. M.; Rodrigues, A. E., Process development for dimethylacetal synthesis: Thermodynamics and reaction kinetics. *Industrial & engineering chemistry research* 2005, *44* (19), 7287-7297.

[7] Suresh Kumar Reddy, K.; Sreedhar, I.; Vijaya Raghavan, K., Kinetic studies on vapour phase pyridine synthesis and catalyst regeneration studies. *The Canadian Journal of Chemical Engineering* 2011, *89* (4), 854-863.

[8] Shiau, C.-Y.; Chen, S.; Tsai, J.; Lin, S., Effect of zinc addition on copper catalyst in isoamyl alcohol dehydrogenation. *Applied Catalysis A: General* 2000, *198* (1), 95-102.

[9] Blanch, G. P.; Reglero, G.; Herraiz, M., Rapid extraction of wine aroma compounds using a new simultaneous distillation-solvent extraction device. *Food chemistry* 1996, *56* (4), 439-444.

[10] López, E. F.; Gómez, E. F., Comparison of solvents for determination of monoterpenes in wine using liquid-liquid extraction. *Chromatographia* 2000, *52* (11-12), 798-802.

[11] Seader, J., *Separation process principles*. Wiley. com: 2006.

[12] Wennekes, W. B., *Adhesion of RFL-treated cords to rubber: new insights into interfacial phenomena*. University of Twente: 2008.

[13] Berg, L.; Yang, Z., Separation of pyridine from water by extractive distillation. Google Patents: 1992.