Production of Acetic Acid from the Monsanto Process.

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Certificate

This is to certify that work in this thesis has been carried out by **Ms. Hijab Hassan, Mr. Ahmad Maqsood** and **Mr. Uzair Asad,** completed under my supervision in School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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Dedication

To our parents, to our teachers, to our friends, and to SCME.

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Abstract

Acetic acid is a clear, colourless, corrosive liquid that has a pungent odour and is a dangerous vesicant. It has pungent vinegar like odour. Mostly, acetic acid is manufactured by methanol carbonylation, direct oxidation of n-butane and direct oxidation of ethylene. The total worldwide production of virgin acetic acid is estimated at 5MMTPA (million metric tons per year). Acetic acid is used in the manufacture of a wide range of polymers like PVA (poly vinyl acetate), adhesives etc. It is also used in the manufacture of bleaching agents, pharmaceutical products and agro-chemicals. The Monsanto process is studied in depth for this project. Methanol Carbonylation (Monsanto Process) was initiated in 1960 by BASF. The raw materials used for this process are Carbon Monoxide and Methanol. The optimum conditions for this process are 180°C-220°C temperature, 30-40 atm pressure and Rhodium catalyst with hydrogen iodide as promoter. Due to high selectivity of raw materials, the finals products are of great purity. The Monsanto process is designed and optimized for this project. It is studied in depth and simulated using Aspen Hysys. Research is being done on Lithium based promoters to reduce operating temperatures to under 120℃. In the future, a reactive distillation scheme may be developed to integrate all plant units into one main vessel.

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Chapter 1: Introduction.

1.1 Introduction.

Acetic acid is the world's most consumed chemical with a demand of 6.4 million tonnes in 2015. The total worldwide production of virgin acetic acid is estimated at 5MMTPA (million metric tons per year). The global market of acetic acid is expected to be a worth of $13 billion by 2021. The major end user product produced through acetic acid processing is the Vinyl Acetate, which is the base product of many industrial and consumer products. This is extensively used in paint products, coating material, textile industry and adhesives. Vinyl Acetate accounted for thirty per cent of the acetic acid market share. With a rise in the demand of Vinyl Acetate in the global market, the acetic acid demand is expected to increase rapidly in the coming years.

Acetic acid is an organic compound and is also called the ethanoic or formic acid. It is a colourless and transparent liquid with corrosive properties. It has a pungent smell like that of vinegar and is known to cause blistering. Acetic acid is commonly found in brine found in oil fields, the sea waters, rain and some amount are also found in living beings but this is a trace quantity. The following physical properties are observed in acetic acid:

Table 1 Physical Properties of Acetic Acid.

Physical Property.	
Molecular mass.	60.05 g/mol
Density at 25℃.	1.049 g/cm^{-3}
Melting Point.	16.6 ℃
Boiling Point.	118 ℃
Flash Point.	39℃
Vapour Pressure at 25℃.	15.7 mm Hg
Viscosity at 25℃.	1.056 mPa-s
pH.	2.4
Heat of Combustion.	874.2 kJ/mol
Heat of Vaporisation at 25℃.	23.36 kJ/mol
Critical Temperature	321.6℃
Critical Pressure	57.86 KPa

Mostly, acetic acid is manufactured by methanol carbonylation, direct oxidation of n-butane and direct oxidation of ethylene. This will be discussed later on in more detail.

1.2 Uses.

Acetic acid is widely used in the production of many chemical compounds. Acetic acid is most extensively used in the manufacture of Vinyl Acetate. Other than that, it is also used in the production of esters and acetic anhydride. Vinegar production is also a use of this acid; however, the volume of production is relatively low when compared to other chemical compounds.

Acetic acid is used in the following:

- Vinyl Acetate, which is the base product of many industrial and consumer products. This is extensively used in paint products, coating material, textile industry and adhesives.
- Acetate fibres from cellulose acetate. Cellulose acetate is produced from acetic anhydride. This is majorly used in the wide scale production of film used for photography. Acetic anhydride is also used in the formation of drugs like heroin and paracetamol.
- Ester formation for solvents and other organic synthesis processes.
- Glacial acetic acid is used as a solvent as well.
- Vinegar used as a food additive. Vinegar mostly consists of about five to twenty per cent acetic acid by mass and water.
- Acetic acid also has significant applications in the medical field. Direct injection into malignant tumours is used as a treatment for various cancers like cervical cancer. It is used as an antiseptic and to treat skin infections effectively.
- It is used to remove scales form objects. Mostly scaling caused by calcium carbonate deposits is easily dissolved by acetic acid.

1.3 Methods for Acetic Acid Production.

Acetic acid is produced in the industry through biological and synthetic processes. Through biological process like fermentation in the presence of microorganisms, only ten per cent of the global demand is met. The major demand is satisfied using the carbonylation process of about seventy-five per cent. Two major industrial companies are dominant in the acetic acid market. BP Chemicals and Celanese play a major role in providing virgin acetic acid globally. The major processes involved in the manufacture of acetic acid are discussed below.

1.3.1. Monsanto Process.

The Monsanto process is one of the oldest process for acetic acid production. It was started by the BASF in Germany in the year 1960. The Monsanto process also known as the methanol carbonylation process use the initial feedstock of methanol and carbon monoxide. The process is carried out at temperatures of 180°C-220°C and pressures of 30-40 atm in the presence of a rhodium catalyst with the addition of hydrogen iodide as a promoter. The final product produced is highly pure i.e. ninety-nine per cent. The yield produced from this process based on methanol alone is ninety-nine per cent, which is very high compared to other processes.

Methanol and carbon monoxide are fed into a continuously stirred reactor where the react to produce acetic acid and other by products. This product stream is to be purified. For this, the products pass through a series of distillation columns to achieve the required purity. Gases produced from the reaction are continuously recycled to maintain their levels in the reaction vessel. This is to make sure that the catalyst complexes formed remain stable. Moreover, water levels are kept at a constant level of fourteen to fifteen weight per cent to ensure stability of catalysts complex.

1.3.2. Cativa Process.

Cativa process is the modified form of Monsanto process, developed by BP in 1996, with Iridium catalyst and Ruthenium as promoter. Cativa process is almost similar to Monsanto process with reduced number of equipment.

1.3.3. Transition Metals.

Direct oxidation of n-butane produces nine per cent of the total acetic acid globally produced. The catalyst used in this process are Cobalt Acetate and Manganese Acetate. The product produced consists of is as propionic acid, acetone and acetic acid. This method is useful when production of multiple acids is required.

1.3.4. Process Selection.

The methanol carbonylation, direct oxidation of n-butane and direct oxidation of ethylene are the three most widely implemented methods to manufacture acetic acid.

Methanol carbonylation also known as the "Monsanto process" was initially developed by BASF in 1960. The process operates at 180-220°C and 30-40 atm via the use of a rhodium catalyst, leading to energy costs set to a bare minimum. Although it operates at such low operating conditions, the process provides with high selectivity of acetic acid. The final product holds great purity due to the selectivity of methanol and carbon monoxide, which are 99% and 90% respectively. The process outlines continuous supply of methanol and carbon monoxide into the reactor. The combination of exhaust gas produced from the reactor and purification section are recovered as light-ends and recycled back into the reactor. Consequently, the acetic acid produced from the reactor is separated as a side-cut and delivered to the dehydration column. Acetic acid and water mixture are then released at the top of the column and back to the reactor while propionic acid is taken to the subsequent column. Further purification takes place and acetic acid is generated as a side-cut. Continuous recycling of overhead and bottoms found in fractional column into reactor takes place.

The main raw materials for this process are methanol and carbon monoxide. In the reaction process, methyl iodide is added to the rhodium complex, which consecutively migrates to a carbonyl group and reacts with CO to form the rhodium-acetyl complex. The excess water readily hydrolyses the acetyl iodide (CH_3COI) to produce acetic acid and hydrogen iodide in order to complete the catalytic cycle. However, a quantity of water (14-15 wt.%) is required in order to maintain stability and activity of the catalyst, thus separation of water from acetic acid requires excessive amount of energy, further limiting storage capacity. Methanol carbonylation produces propionic acid as the major by-product of this process, present as an impurity in methanol feed. In order to lower the yield of propionic acid produced, it is suggested to decrease the amount of acetaldehyde produced by the rhodium catalyst.

The direct oxidation of hydrocarbons route occurs through pumping of an ethane and oxygen mixture at 515 K and 16 bars in a multi-tubular reactor. The product formed is cooled to 303 K via two steps, initially through formation of high-density steam and subsequent separation of formed gas and liquid mixture in a flash. The acetic acid-water mixture produced is then separated in a rectification column and pure acetic acid is generated as the bottom product. The resulting gaseous stream, made up of ethane, ethylene and CO_2, is recycled back into the system. CO_2 is separated into an absorber, while ethylene and ethane are put back into the feed gas. Nonetheless, the oxidation of n-butane requires large amounts of water and generates a dilute acetic acid solution of which concentration is highly energy intensive, as a result the yield of acetic acid produced is lower than the one obtained in other processes. A vast number of by-products are formed, some of which are propionic and formic acids. Furthermore, this particular process requires large quantities of water, hence water gas shift reaction is a major drawback as extensive CO_2 is produced as a result. In essence, the oxidation of hydrocarbons process is cheaper to run as a result of its feedstock, but at the cost of being less efficient as it produces more waste and a lower grade chemical. Flexibility in the process allows it to produce a purer acetic acid with high selectivity, however extensive operation expenses are necessary.

The production of acetic acid through direct oxidation of ethylene was first proposed by Showa Denko K.K. The process occurs through the mixture of ethylene and oxygen in their vapour phases at 160-210°Cover a solid catalyst, the acetic acid generated is of high selectivity. The reaction is initiated from the cooling of gas produced in the reactor to ambient temperature, where the products of acetic acid, water and other organic compounds are condensed and separated. The condensate transfers to the crude acetic acid tank, while the compressor pressurizes the un-condensed gas back to the reactor. Light-end products such as acetaldehyde, ethyl acetate and ethanol are removed through distillation, allowing acetic acid and light-ends compounds to migrate to the purification section where pure acetic acid is produced. This process produces large amounts of heat which is recovered as steam and used in the purification section as a source of heat. The process meets the requirements of being both competitive and environmentally friendly. Although it rivals methanol carbonylation, the process is only efficient with smaller plants of about (100-250 kt/a) and considering the fact that the feedstock price of ethylene is more expensive than raw materials used in the other processes mentioned, thus economically it will not be as profitable as the methanol carbonylation process given that the selectivity of both is of 90%.

Overall, the methanol carbonylation process is highly efficient in that it produces acetic acid with more sought-after selectivity and purity. The oxidation of ethylene is more environmentally friendly; however, it can only be operated for a capacity of up to 200 ,000 tonnes per year and the oxidation of hydrocarbons is cheaper to run but does not produce a pure acetic acid product. The oxidation of hydrocarbons highly affects the environment as a result of its emissions of CO2, whilst both the ethylene oxidation and methanol carbonylation don't pose much threat to the environment, the latter is still more environmentally friendly as it produces less waste and recycles most of its reactants. This enables the process to be continuous and thus economically beneficial.

Chapter 2: Process Flow Diagram.

This chapter deals with the flow diagram that is used in this project.

2.1 Process Flow Sheet.

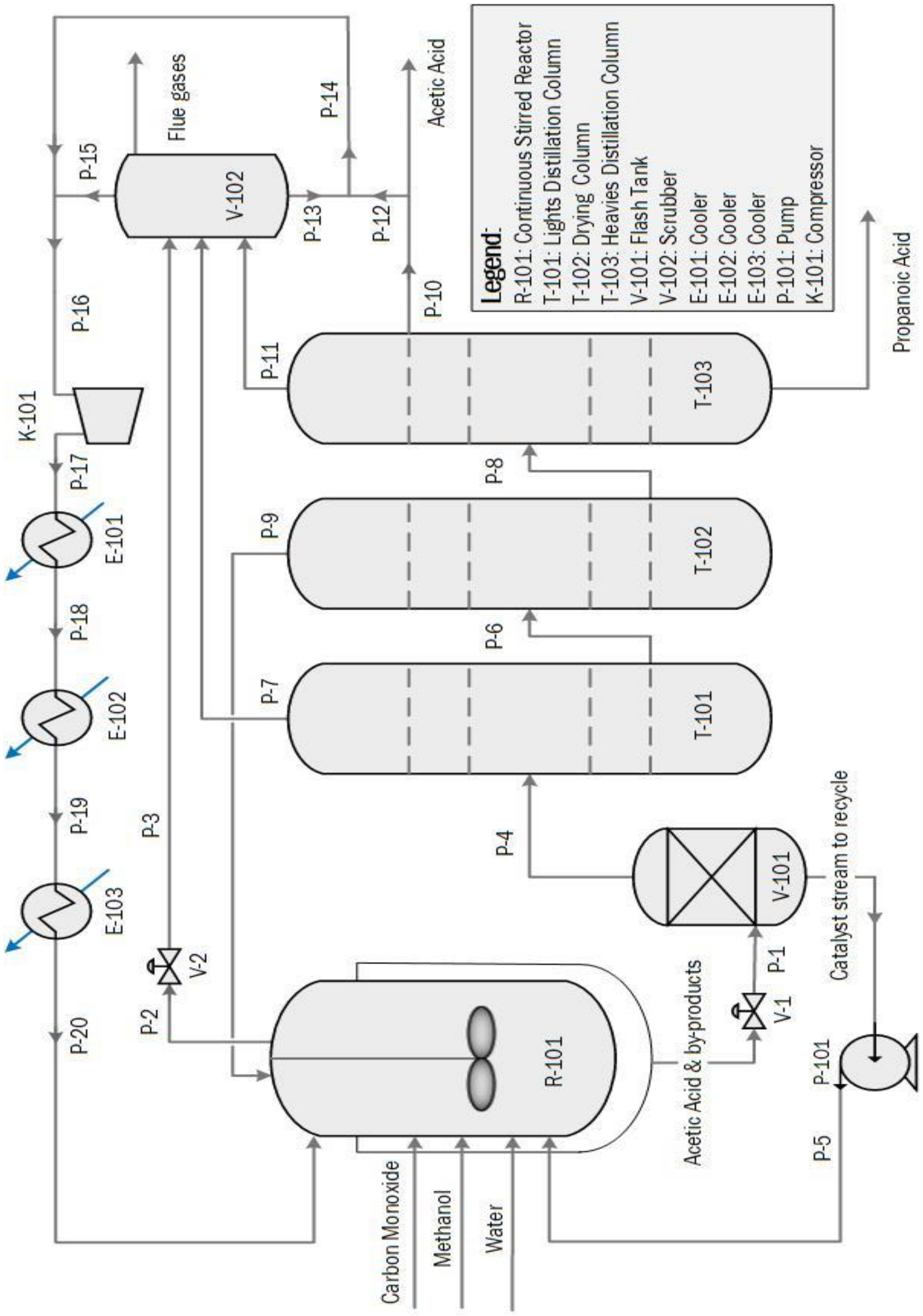

Figure 1.1 PFD of the Monsanto Process.

2.2 Process Description.

The acetic acid process stream needs to have 400 ppm of propanoic acid and less than 1500 ppm of water. Carbon monoxide and methanol are added to a continuous stirred reactor where they react in the presence of Rhodium catalyst to produce acetic acid and by-products like propanoic acid, methyl acetate etc. The liquid product mixture leaves the reactor zone and enters into the flash zone where the liquid and vapour phases are separated. The liquid phase mainly consists of the catalyst complex of Rhodium, whereas the vapour phase consists of the acetic acid, propanoic acid, methyl acetate, unreacted methanol etc. The vapour phase is sent into the distillation column train where propanoic acid is withdrawn from the bottom and the top stream goes into the scrubber. Here, the flue gases and acetic acid are the main products and the rest of the unreacted material is sent back to the reactor. The acetic acid produced is about 95% pure.

Chapter 3: Material Balance.

The chapter discusses the masses moving in and out through various equipment. Mass balance calculations are employed to find the required masses in each stream. All balances have been verified through Aspen Hysys simulation.

3.1 Overall Balances.

Formula used:

$$\text{Molar Flow Rate In} - \text{Molar Flow Rate Out} + \text{Molar Generation Rate} = \text{Molar Accumulation Rate}$$

Table 1 Overall Balance Sheet.

Stream	Carbon monoxide	Methanol	Water	Acetic Acid and by-products	P-4	P-6	P-8	Propanoic Acid	Acetic Acid	Flue Gases
Mass Flow Rates (kg/hr)										
Methanol	0.000	27,040	0.000	90.05	90.04	0.000	0.000	0.000	0.000	91.864
Carbon monoxide	25,210	0.000	0.000	1474	1474	0.000	0.000	0.000	0.000	1504
Water	0.000	0.000	720.4	968.4	871.6	192.8	79.81	0.000	40.25	622.7
Acetic Acid	0.000	0.000	0.000	99,270	98,340	98,010	69,360	290.5	49530	0.000
Carbon dioxide	0.000	0.000	0.000	204.0	204.01	0.000	0.000	0.000	0.000	208.2
Propanoic Acid	0.000	0.000	0.000	428.3	428.30	428.3	423.4	382.3	17.21	24.92
Hydrogen	0.000	0.000	0.000	9.345	9.345	0.000	0.000	0.000	0.000	9.536
Ethanol	0.000	273.1	0.000	9.570	9.570	0.000	0.000	0.000	0.000	9.754
Rhodium Catalyst	0.000	0.000	0.000	1021	0.000	0.000	0.000	0.000	0.000	0.000
Methyl Acetate	0.000	0.000	0.000	386.6	386.6	0.000	0.000	0.000	0.000	394.5
Methyl Iodide	0.000	0.000	0.000	6.626	4.969	0.000	0.000	0.000	0.000	5.105

3.2 Reactor.

Material Balance:

$$F_{in} - F_{out} + \int r \, dV = \frac{dN}{dt}$$

Continuously stirred tank reactor (well mixed):

$$\text{Molar Flow Rate In} - \text{Molar Flow Rate Out} + \text{Molar Generation Rate} = 0$$

$$F_{in} - F_{out} + rV = 0$$

3.2.1 Balance Data:

Table 2 Reactor Material Balance Sheet.

Carbon Monoxide (25,210 kg/hr, 25.00°C, 31 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
CO	1.00	25,210
Methanol (27,320 kg/hr, 25.53°C, 31 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Methanol	0.99	27,040
Ethanol	0.01	273.10
Water (720.4 kg/hr, 26.87°C, 31 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Water	1.00	720.4
P-9 (28,760 kg/hr, 117.1°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Water	0.0039	113.5
Acetic Acid	0.9959	28,640

Propanoic Acid	0.0002	4.843
P-5 (11,030 kg/hr, 104.5°C, 31 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Water	0.0088	97.16
Acetic Acid	0.8906	9,922
Methyl Iodide	0.0006	6.761
Rhodium Catalyst	0.1000	1,021
P-20 (26,230 kg/hr, 69.71°C, 59 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Water	0.0021	46.43
Acetic Acid	0.9975	26,180
Propanoic Acid	0.0004	8.681
P-1 (112,800 kg/hr, 160.0°C, 31 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.8683	99,270
Water	0.0086	968.4
Propanoic Acid	0.0038	428.3
Methanol	0.0008	90.05
CO	0.0131	1474
Ethanol	0.0001	9.570
Carbon dioxide	0.0018	204.0
Hydrogen	0.0001	9.345

Methyl Acetate	0.0034	386.6
Methyl Iodide	0.0001	6.626
Rhodium Catalyst	0.1000	1021
P-2/P-3 (2,303 kg/hr, 160.0°C, 31 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Water	0.0086	19.76
Acetic Acid	0.9683	22,30
Propanoic Acid	0.0038	8.741
Methanol	0.0008	1.838
CO	0.0131	30.09
Ethanol	0.0001	0.1953
Carbon dioxide	0.0018	4.163
Hydrogen	0.0001	0.1907
Methyl Acetate	0.0034	7.890
Methyl Iodide	0.0001	0.1352

3.3 Flash Tank.

Formula used:

$$\text{Molar Flow Rate In} - \text{Molar Flow Rate Out} + \text{Molar Generation Rate} = \text{Molar Accumulation Rate.}$$

3.3.1 Balance Data:

Table 3 Flash Tank Material Balance Sheet.

P-1 (112,800 kg/hr, 160.0°C, 31 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**

Acetic Acid	0.8683	99,270
Water	0.0086	968.4
Propanoic Acid	0.0038	428.3
Methanol	0.0008	90.05
CO	0.0131	1474
Ethanol	0.0001	9.570
Carbon dioxide	0.0018	204.0
Hydrogen	0.0001	9.345
Methyl Acetate	0.0034	386.6
Methyl Iodide	0.0001	6.626
Rhodium Catalyst	0.1000	1021
P-4 (101,800 kg/hr, 104.5°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.9658	98,340
Water	0.0086	871.5
Propanoic Acid	0.0042	428.3
Methanol	0.0009	90.04
CO	0.0145	1474
Ethanol	0.0001	9.571
Carbon dioxide	0.0020	204.1
Hydrogen	0.0001	9.345
Methyl Acetate	0.0038	386.6

Catalyst stream to recycle (11,030 kg/hr, 104.5°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.8911	10,350
Water	0.0088	96.84
Methyl Iodide	0.0002	1.657
Rhodium Catalyst	0.1000	1,021

3.4 Lights Distillation Column.

Formula used:

$$\text{Molar Flow Rate In} - \text{Molar Flow Rate Out} + \text{Molar Generation Rate} = \text{Molar Accumulation Rate.}$$

3.4.1 Balance Data:

Table 4 Lights Distillation Column Material Balance Sheet.

P-4 (101,800 kg/hr, 104.5°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.9658	98,340
Water	0.0086	871.5
Propanoic Acid	0.0042	428.3
Methanol	0.0009	90.04
CO	0.0145	1474
Ethanol	0.0001	9.572
Carbon dioxide	0.0020	204.1
Hydrogen	0.0001	9.345
Methyl Acetate	0.0038	386.6
P-6 (98,630 kg/hr, 117.2°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.9900	98,010

Water	0.0065	192.7
Propanoic Acid	0.0035	428.3
P-7 (3,191 kg/hr, 76.20°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.1044	333.2
Water	0.2127	678.7
Methanol	0.0282	92.12
CO	0.4620	1474
Ethanol	0.0001	9.552
Carbon dioxide	0.0639	204.1
Hydrogen	0.0029	9.345
Methyl Acetate	0.1212	386.6
Methyl Iodide	0.0016	4.969

3.5 Drying Column.

Formula used:

$$\text{Molar Flow Rate In} - \text{Molar Flow Rate Out} + \text{Molar Generation Rate} = \text{Molar Accumulation Rate.}$$

3.5.1 Balance Data:

Table 5 Drying Column Material Balance Sheet.

P-6 (98,630 kg/hr, 117.2°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.9900	98,010
Water	0.0065	192.7

Propanoic Acid	0.0035	428.3
P-8 (69,870 kg/hr, 117.4°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.9928	69,360
Water	0.0011	79.81
Propanoic Acid	0.0061	423.4
P-9 (28,760 kg/hr, 117.1°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Water	0.0039	113.5
Acetic Acid	0.9959	28,640
Propanoic Acid	0.0002	4.843

3.6 Heavies Distillation Column.

Formula used:

$$\text{Molar Flow Rate In} - \text{Molar Flow Rate Out} + \text{Molar Generation Rate} = \text{Molar Accumulation Rate.}$$

3.6.1 Balance Data:

Table 6 Heavies Distillation Column Material Data Sheet.

P-8 (69,870 kg/hr, 117.4°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.9928	69,360
Water	0.0011	79.81
Propanoic Acid	0.0061	423.4
P-10 (69,200 kg/hr, 117.4°C, 1 bar)		

Component	Mass Fraction	Mass Flow rate (kg/hr)
Acetic Acid	0.9983	69,070
Water	0.0012	79.81
Propanoic Acid	0.0006	41.09
Propanoic acid (672.9 kg/hr, 117.4°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.4318	290.5
Propanoic Acid	0.5682	382.3
Acetic Acid (49,630 kg/hr, 117.4°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.9975	49530
Water	0.0022	40.25
Propanoic Acid	0.0003	17.21
P-12 (19570 kg/hr, 117.4°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.9975	19540
Water	0.0022	38.75
Propanoic Acid	0.0003	24.21

3.7 Absorption Column.

Formula used:

$$\text{Molar Flow Rate In} - \text{Molar Flow Rate Out} + \text{Molar Generation Rate} = \text{Molar Accumulation Rate.}$$

3.7.1 Balance Data:

Table 7 Absorption Column Material Data Sheet.

P-2/P-3 (2,303 kg/hr, 160.0°C, 31 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Water	0.0086	19.76
Acetic Acid	0.9683	22,30
Propanoic Acid	0.0038	8.741
Methanol	0.0008	1.838
CO	0.0131	30.09
Ethanol	0.0001	0.1953
Carbon dioxide	0.0018	4.163
Hydrogen	0.0001	0.1907
Methyl Acetate	0.0034	7.890
Methyl Iodide	0.0001	0.1352
P-7 (3,191 kg/hr, 76.20°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.1044	333.2
Water	0.2127	678.7
Methanol	0.0282	92.12
CO	0.4620	1474
Ethanol	0.0001	9.552
Carbon dioxide	0.0639	204.1
Hydrogen	0.0029	9.345
Methyl Acetate	0.1212	386.6
Methyl Iodide	0.0016	4.969
P-12 (19,570 kg/hr, 117.4°C, 1 bar)		

Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.9975	19,540
Water	0.0022	38.75
Propanoic Acid	0.0003	24.21
P-13 (2,908 kg/hr, 190.4°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.8249	2731
Water	0.1740	172.8
Propanoic Acid	0.0011	4.428
P-14 (26,270 kg/hr, 125.9°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Acetic Acid	0.9744	26,050
Water	0.0251	201.1
Propanoic Acid	0.0006	18.17
P-14 (2871 kg/hr, 60.0°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Water	0.2169	622.69
Propanoic Acid	0.0087	24.917
Methanol	0.0320	91.864
CO	0.5240	1504.4
Ethanol	0.0034	9.7536
Carbon dioxide	0.0725	208.17

Hydrogen	0.0033	9.5359
Methyl Acetate	0.1375	394.51
Methyl Iodide	0.0018	5.1049
Flue Gases (2871 kg/hr, 60.0°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Water	0.2169	622.69
Propanoic Acid	0.0087	24.917
Methanol	0.0320	91.864
CO	0.5240	1504.4
Ethanol	0.0034	9.7536
Carbon dioxide	0.0725	208.17
Hydrogen	0.0033	9.5359
Methyl Acetate	0.1375	394.51
Methyl Iodide	0.0018	5.1049

3.8 Utilities.

Formula used:

$$\text{Molar Flow Rate In} - \text{Molar Flow Rate Out} + \text{Molar Generation Rate} = \text{Molar Accumulation Rate.}$$

3.8.1 Balance Data:

Table 8 Utilities Material Balance Sheet.

P-16/17/18/19 (26,230 kg/hr, 125.9°C, 1 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Water	0.0021	46.43

Acetic Acid	0.9975	26,180
Propanoic Acid	0.0004	8.681
P-26 (26,230 kg/hr, 69.71°C, 59 bar)		
Component	**Mass Fraction**	**Mass Flow rate (kg/hr)**
Water	0.0021	46.43
Acetic Acid	0.9975	26,180
Propanoic Acid	0.0004	8.681

Chapter 4: Energy Balance.

The chapter discusses the energy moving in and out through various equipment systems. Energy balance calculations are employed to find the required enthalpies in each stream. All balances have been verified through Aspen Hysys simulation.

4.1 Overall Balances.

Formulae used:

1. $Q = mc_p\Delta T$
2. $\sum Q_{in} = \sum Q_{out}$

Table 9 Overall Energy Balance.

Stream	Carbon monoxide	Methanol	Water	Acetic Acid and by-products	P-6	P-8	Propanoic Acid	Acetic Acid	Flue Gases
Enthalpy (KJ/Kmol)	-265,600	-239,600	284,700	-102,900	-447,700	-435,800	-463,500	-450,020	-188,700
Temperature (°C)	25.00	25.00	26.83	160.0	104.5	104.5	117.4	117.4	60.00
Pressure (bar)	31.00	31.00	31.00	31.00	1.000	1.000	1.000	1.000	1.000

4.2 Reactor.

The reaction is exothermic in nature so a large amount of heat is released into the environment.

4.2.1 Reaction Kinetics

Acetic acid production process run by methanol carbonylation consists of three sections. In the reaction section acetic acid is produced through continuous reaction of carbon monoxide and methanol in a mechanically agitated gas-liquid reactor at approximately 185 °C and 28.6 bar. A soluble catalyst system consisting of a rhodium complex (catalyst) and methyl iodide-hydrogen iodide (the promoter) make the reaction to occur at a reasonable rate.

There are three primary reactions which occur in the acetic acid process:

1. Carbonylation reaction.

$$CO + CH_3OH \rightarrow CH_3COOH$$

Rate's equation for this reaction is:

$$\mathrm{Rate} = 156664276 \times \exp\left(-\frac{71407}{RT}\right)[I]^{1.055}[Rh]^{1.0096}$$

2. Water gas shift equation.

$$CO + H_2O \rightarrow CO_2 + H_2$$

Rate's equation for this reaction is:

$$\mathrm{Rate} = 146664 \times \exp\left(-\frac{71407}{RT}\right)[I]^{1.055}[Rh]^{1.0096}$$

[I] and [Rh] in the 2 equations above are molar concentration of methyl iodide and rhodium in

kmol/m^3, respectively.

3. By-products reaction.

$$CH_3CH_2OH + CO \rightarrow CH_3CH_2COOH$$

$$CH_3COOH + 2H_2 \rightarrow H_3CH_2OH + H_2O$$

The conversion of the carbonylation reaction is high (99.4%) and completely converts the methanol. The acetic acid process does not produce significant volumes of by-products. The major by-product is propionic acid.

4.2.2 Balance Data sheet.

Formulae used:

1. $Q = mc_p\Delta T$
2. $\sum Q_{in} = \sum Q_{out}$
3. $\Delta H^O = \Sigma\, n\Delta H_f{}^O(\mathrm{products}) - \Sigma\, n\Delta H_f{}^O(\mathrm{reactants})$.

Table 10 Standard heat of formations of Reactor components.

Component	Standard Heat of formation (kJ/mol)
Acetic Acid	-483.5
Water	-286.0
Methanol	-283.6
Propanoic Acid	-1527.2
Methyl Acetate	-298.15
Methyl Iodide	14.92
Carbon dioxide	-393.5

Table 11 Reactor Energy Balance Sheet.

<table>
<tr><th colspan="3">Carbon Monoxide (25,210 kg/hr, 25°C, 31 bar)</th></tr>
<tr><th>Molar Flow (kmol/hr)</th><th>Molar Enthalpy (kJ/kmol)</th><th>Total Energy (kJ/hr)</th></tr>
<tr><td>2,831</td><td>-265,600</td><td>-7.519×10^{8}</td></tr>
<tr><th colspan="3">Methanol (27,320 kg/hr, 25.53°C, 31 bar)</th></tr>
<tr><th>Molar Flow (kmol/hr)</th><th>Molar Enthalpy (kJ/kmol)</th><th>Total Energy (kJ/hr)</th></tr>
<tr><td>850</td><td>-239,600</td><td>-2.036×10^{8}</td></tr>
<tr><th colspan="3">Water (720.4 kg/hr, 26.87°C, 31 bar)</th></tr>
<tr><th>Molar Flow (kmol/hr)</th><th>Molar Enthalpy (kJ/kmol)</th><th>Total Energy (kJ/hr)</th></tr>
<tr><td>40</td><td>-284,700</td><td>-1.139×10^{7}</td></tr>
<tr><th colspan="3">P-9 (28,760 kg/hr, 117.1°C, 1 bar)</th></tr>
<tr><th>Molar Flow (kmol/hr)</th><th>Molar Enthalpy (kJ/kmol)</th><th>Total Energy (kJ/hr)</th></tr>
<tr><td>483</td><td>-448,300</td><td>-2.165×10^{8}</td></tr>
<tr><th colspan="3">P-5 (11,030 kg/hr, 104.5°C, 31 bar)</th></tr>
</table>

Molar Flow (kmol/hr)	Molar Enthalpy (kJ/kmol)	Total Energy (kJ/hr)
187.3	-447,800	-8.387×10^{7}
P-20 (22,120 kg/hr, 69.71°C, 59 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
370	-455,200	-1.684×10^{8}
P-2/P-3 (2,303 kg/hr, 160°C, 31 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
39.78	-431,600	-1.716×10^{7}
Acetic Acid and by-products (112,800 kg/hr, 160°C, 31 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
2033	-102,900	-2.093×10^{8}

4.3 Flash Tank.

Formulae used:

1. $Q = mc_p\Delta T$
2. $\sum Q_{in} = \sum Q_{out}$

4.3.1 Balance Data sheet.

Table 12 Flash Tank Energy Balance Sheet.

P-1 (112,800 kg/hr, 104.5°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
1950	-436,900	-8.516×10^{8}

P-4 (101,800 kg/hr, 104.5°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
1760	-435,800	-7.679×10^{8}
Catalyst stream to recycle (11,030 kg/hr, 104.5°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
187.3	-447,700	-8.387×10^{7}

4.4 Lights Distillation Column.

Formulae used:

1. $Q = mc_p\Delta T$
2. $\sum Q_{in} = \sum Q_{out}$

4.4.1 Balance Data sheet.

Table 13 Lights Distillation Column Energy Balance Sheet.

P-4 (101,800 kg/hr, 104.5°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
1760	-435,800	-7.679×10^{8}
P-6 (98,630 kg/hr, 117.2°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
113	-192,300	-2.173×10^{7}
P-7 (3,191 kg/hr, 76.20°C, 1 bar)		

Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
1649	-450,500	-7.679×10^{8}

Condenser duty: 1.395×10^{8} kJ/hr.
Reboiler duty: 1.432×10^{8} kJ/hr.

4.5 Drying Column.

Formulae used:

1. $Q = mc_p\Delta T$
2. $\sum Q_{in} = \sum Q_{out}$

4.5.1 Balance Data sheet.

Table 14 Drying Column Energy Balance Sheet.

P-6 (98,630 kg/hr, 117.2°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
113	-192,300	-2.173×10^{7}
P-8 (69,870 kg/hr, 117.4°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
1165	-451,074	-5.255×10^{8}
P-9 (28,760 kg/hr, 117.1°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
483	-448,300	-2.165×10^{8}

Condenser duty: 7.589×10^{4} kJ/hr.

Reboiler duty: 6.198×10^{5} kJ/hr.

4.6 Heavies Distillation Column.

Formulae used:

1. $Q = mc_p\Delta T$
2. $\sum Q_{in} = \sum Q_{out}$

4.6.1 Balance Data sheet.

Table 15 Heavies Distillation Column Energy Balance Sheet.

P-8 (69,870 kg/hr, 117.4°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
1165	-451,074	-5.255×10^{8}
P-10 (69,200 kg/hr, 117.4°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
1218	-450,210	-5.288×10^{8}
Propanoic Acid (672.9 kg/hr, 117.4°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
10	-463,500	-4.635×10^{6}
Acetic Acid (49,630 kg/hr, 117.4°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
827.4	-450,020	-3.752×10^{8}
P-12 (19570 kg/hr, 117.4°C, 1 bar)		
Molar Flow	**Molar Enthalpy (kJ/kmol)**	**Total Energy**

(kmol/hr)		(kJ/hr)
310.1	-450,020	-1.768×10^{8}

Condenser duty: 9.975×10^{4} kJ/hr.

Reboiler duty: 1.044×10^{6} kJ/hr.

4.7 Absorption Column.

Formulae used:

1. $Q = mc_p\Delta T$
2. $\sum Q_{in} = \sum Q_{out}$

4.7.1 Balance Data sheet.

Table 16 Absorption Column Energy Balance Sheet.

P-2/P-3 (2,303 kg/hr, 160°C, 31 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
39.78	-431,600	-1.716×10^{7}
P-7 (3,191 kg/hr, 76.20°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
1649	-450,500	-7.679×10^{8}
P-12 (19570 kg/hr, 117.4°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
310.1	-450,020	-1.768×10^{8}
P-13 (2,908 kg/hr, 190.4°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**

55.15	-395,200	-2.176×10^{7}
P-14 (26,270 kg/hr, 125.9°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
445.3	-440,050	-1.974×10^{8}
Flue Gases (2871 kg/hr, 60.0°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
113.4	-188,700	-2.140×10^{7}

4.8 Utilities.

Formulae used:

1. $Q = mc_p\Delta T$
2. $\sum Q_{in} = \sum Q_{out}$
3. $Pump\ W = \frac{V\Delta P(1-\beta T)}{\varepsilon}$
4. $Q = m\hat{h}$

4.8.1 Balance Data sheet.

Table 17 Utilities Energy Balance Sheet.

P-16 (26,230 kg/hr, 125.9°C, 1 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
445.3	-440,050	-1.974×10^{8}
P-17 (26,230 kg/hr, 391.8°C, 59 bar)		
Molar Flow (kmol/hr)	**Molar Enthalpy (kJ/kmol)**	**Total Energy (kJ/hr)**
445.3	-406,700	-1.811×10^{8}

<table>
<tr><th colspan="3">P-18 (26,230 kg/hr, 291.8°C, 59 bar)</th></tr>
<tr><th>Molar Flow (kmol/hr)</th><th>Molar Enthalpy (kJ/kmol)</th><th>Total Energy (kJ/hr)</th></tr>
<tr><td>445.3</td><td>-425,700</td><td>-1.896×10^{8}</td></tr>
<tr><th colspan="3">P-19 (26,230 kg/hr, 191.8°C, 59 bar)</th></tr>
<tr><th>Molar Flow (kmol/hr)</th><th>Molar Enthalpy (kJ/kmol)</th><th>Total Energy (kJ/hr)</th></tr>
<tr><td>445.3</td><td>-439,200</td><td>-1.956×10^{8}</td></tr>
<tr><th colspan="3">P-20 (26,230 kg/hr, 69.71°C, 59 bar)</th></tr>
<tr><th>Molar Flow (kmol/hr)</th><th>Molar Enthalpy (kJ/kmol)</th><th>Total Energy (kJ/hr)</th></tr>
<tr><td>445.3</td><td>-455,200</td><td>-1.984×10^{8}</td></tr>
</table>

Equipment	**Power (kW)**
K-101	4,534
P-101	13.26
Total	**-4,574**

Compressor power: 4,534 kW.

E-101 duty: 8.476×10^{6} kJ/hr.

E-102 duty: 5.995×10^{6} kJ/hr.

E-103 duty: 5.699×10^{6} kJ/hr.

Chapter 5: Equipment Design.

5.1 Reactor.

Feed Composition.

Table 18 Feed Composition in Reactor.

Components	Molar Flow (kgmol/hr)
Methanol	844.02
Carbon monoxide	899.98
Water	39.98

5.1.1 Reactor Volume.

$$\frac{V}{F_{A0}} = \frac{X_A}{-r_A}$$

V is the volume of the reactor.

F_{A0} are the initial moles of feed.

X_A is the conversion.

r_A is the reaction rate.

$$V = \frac{F_{A0}X_A}{-r_A}$$

Total moles of feed = 1783.98 kgmol/hr

$$Total\ volumetric\ flow\ rate\ of\ feed = 34.00 + 31.54 + 0.722$$

$$V_0 = 66.262 \text{ m3/hr}$$

$$C_{A0} = \frac{F_{A0}}{V_0}$$

$$C_{A0} = \frac{1783.98}{66.262}$$

$$C_{A0} = 26.92\ kgmol$$

Therefore, reactor volume will be:

$$V = \frac{F_{A0}X_{RXN}}{-r_A}$$

$$V = \frac{F_{A0}X_{RXN}}{k[C_A]^2}$$

$X_{Methanol} = 0.99$ and $X_{Carbonmonoxide} = 0.90$.

So, $X_{RXN} = 0.95$.

$k = 0.11\ m^3/kgmol\ s$ (From literature).

$$V\ = \frac{F_{A0}X_{RXN}}{k[C_A]^2}$$

$$V\ = \frac{1783.98 * 0.95}{0.11[26.92]^2}$$

$$V\ = 21.26\, m^3$$

5.1.2 Dimensions of reactor.

$$V = \left(\frac{\mathrm{\pi * d^2}}{4}\right) * h$$

Where:

d= diameter of the reactor.

h= height of the reactor.

According to the literature, the height is double of the diameter:

So,

$$V = \left(\frac{\mathrm{\pi * d^2}}{4}\right) * h$$

$$V = \left(\frac{\mathrm{\pi * d^2}}{4}\right) * 2d$$

$$21.26 = \left(\frac{\mathrm{\pi * d^2}}{4}\right) * 2d$$

$$d = 2.83\ m$$

$$h = 4.77\ m$$

5.2 Flash Tank.

Density of vapor = 957 Kg/m^3
Density of liquid = 2700 Kg/m^3

Flow rate of vapor =101,800 kg/hr

Flow rate of liquid = 11,030 kg/hr

Now

$$Vapor\ Liquid\ Separation\ factor\ =\ (fl/fv)/\ (\rho v/\rho l)\ 0.5$$

= 0.10834/0.595

= 0.182

Vapor velocity factor = 0.3 m/s

$$Design\ vapor\ velocity\ =\ Kv * \ \{(pL - pv)/pL\}\ 0.5$$

= 0.4047 m/s

Dividing vapor mass flow rate with the density we get

$$= 28.27/270\ \ = 0.0104m3/s$$

For minimum cross-sectional area

Divide volumetric flow rate with vapor velocity

$$Amin\ =\ VL/UV$$

$$=\ 0.0104m3/0.4047m$$

$$Amin\ =\ 0.0256m2$$

For this area we will calculate the diameter

$$Dmin\ =\ (4\pi A)\ 0.5$$

$$=\ (4 * 3.14 * 0.0256)\ 0.5$$

$$=\ 0.567\ m$$

Adding clearance of 0.15m so

D = 0.717m

Surge time for Monsanto / Cativa process is around 5 minutes

Multiplying this time with volumetric flowrate of liquid to get liquid volume

$$\text{Liquid Volume} =\ VL *\ 300$$

$$=\ 0.001134\ m3/s\ *\ 300$$

$$=\ 0.340\ m3$$

Liquid Height:

$$0.340m3 \ = \ 3.14 \ * \ d^2/4 \ * h$$

$$0.340m^3 = \ 3.14 \ * \ 0.5672/4 \ * h$$

Liquid Height = 1.348 m

Vapor Height:

$$V.H \ = \ 1.5 * D \ + \ 0.4$$

$$= \ (1.5 * 0.717) \ + \ 0.4$$

$$= \ 1.4755m$$

$$Total\ Height \ = \ 1.348m \ + \ 1.4755m$$

$$= \ 2.82m$$

Now for L/D ratio

$$2.82/0.717$$

$$= \ 3.93$$

If the L/D ratio is around 3-5 then vertical flash tank is used.

5.3 Lights Distillation Column.

Antoine Equation:

$$\ln P = A - \frac{B}{T + C}$$

At 104.5 °C:

Acetic Acid:

$$A = 16.808$$

$$B = 3405.57$$

$$C = -56.34$$

$$P = 62.33\ mm\ Hg$$

Methyl Acetate:

$$A = 16.1295$$

$$B = 2601.92$$

$$C = -56.15$$

$$P = 633.676\ mm\ Hg$$

Propanoic Acid:

$$A = 17.3789$$

$$B = 3723.42$$

$$C = -67.48$$

$$P = 18.5438\ mm\ Hg$$

Water:

$$A = 18.3036$$

$$B = 3816.44$$

$$C = -46.13$$

$$P = 101.314\ mm\ Hg$$

Methanol:

$$A = 18.5875$$

$$B = 3626.55$$

$$C = -34.29$$

$$P = 451.55\ mm\ Hg$$

Light Key Component: Water.

Heavy Key Component: Methyl acetate.

$$\alpha_i = \frac{P_i}{P_{HK}}$$

Table 19 Relative Volatilities of Distillation Column Components.

Component	z_f	x_d	x_b	α_i
Acetic Acid	0.925	0.054	0.990	0.983
Propanoic Acid	0.003	0.000	0.003	0.029
Water	0.032	0.367	0.007	0.160
Methanol	0.0018	0.027	0.000	0.713
Methyl Acetate	0.003	0.049	0.001	1.000

Gilliland equation:

$$\frac{N_R}{N_S} = \left[\left(\frac{x_{HK,F}}{x_{LK,F}}\right)\left(\frac{x_{LK,B}}{x_{HK,D}}\right)^2\left(\frac{B}{D}\right)\right]^{0.206}$$

Fenske equation:

$$N_{\min} = \frac{\ln\left(\frac{(Dx_D)(Bx'_B)}{(Dx'_D)(Bx_B)}\right)}{\ln \alpha_{ave}}$$

Underwood equation:

$$(1-q)=\sum_i\left[\frac{\alpha_i x_{f,i}}{\alpha_i-\lambda}\right]$$

Assuming q= 1 (saturated liquid at boiling point)

Substituting values:

$$N_{min} = 14$$

$$R_{min} = 0.19$$

$$R = 0.285$$

$$N_{stages} = 25$$

5.4 Drying Column.

Moles of Feed = 1711 kgmol.

$$z_F = 0.5$$

$$x_d = 0.99$$

$$x_b = 0.385$$

$$D = 483.3\ kgmol$$

$$B = 1227\ kgmol$$

$$R = 0.1655$$

$$Y_{intercept} = \frac{x_D}{R+1}$$

$$Y_{intercept} = 0.113$$

5.4.1 Number of stages.

Using McCabe Thiele method:

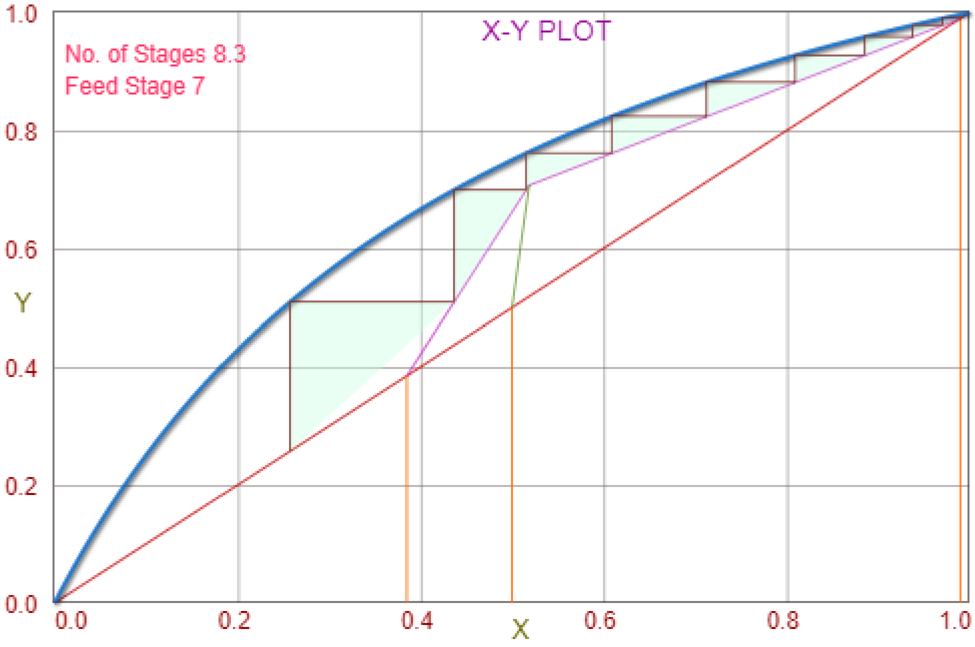

Figure 5.1 Number of plates for drying column.

$$Number\ of\ stages = 9 + 1\ reboiler$$

$$Number\ of\ stages = 10$$

Actual number of stages:

$$N_{actual} = \frac{N_{theoretical}}{\varepsilon}$$

$\varepsilon = 0.50$ from literature.

$$N_{actual} = \frac{10}{0.5}$$

$$N_{actual} = 20$$

Height of tower:

Tray spacing assumed to be 0.7 m

$$H_{tower} = 2.3 * N_{actual}$$

$$H_{tower} = 2.3 * 20$$

$$H_{tower} = 46\ ft\ or\ 14\ m$$

5.4.2 Vapour Velocity.

$$U_v = K(\frac{\rho_L - \rho_v}{\rho_v})^{0.5}$$

$$K = 0.17T^2 + 0.27T - 0.047$$

$$T = 0.701$$

$$K = 209.67.$$

$$U_v = 3066.07\ m/s$$

5.4.3 Diameter of tower.

$$D_{min} = (\frac{4V}{\pi * \rho_v * U_v})^{0.5}$$

$$D_{min} = 1.8\ m$$

Safety considerations:

$$D = 1.05 * 1.8\ m$$

$$D = 1.85\ m$$

5.5 Heavies Distillation Column.

5.5.1 Number of stages.

Using Smoker's equation for number of stages:

Moles of Feed = 1227 kgmol.

$$z_f = 0.9932$$

$$x_d = 0.9999$$

$$x_b = 0.3248$$

$$D = 1217 kgmol$$

$$B = 9.999\ kgmol$$

$$R = 17$$

Rectifying Section:

$$s = \frac{R}{R+1}$$

$$s = 0.9444$$

$$b = \frac{x_d}{R+1}$$

$$b = 0.00556$$

$$s(\alpha - 1)k^2 + [s + b\,(\alpha - 1) - \alpha]k + b = 0$$

$$k = 0.046$$

$$x_0^* = x_d - k$$

$$x_0^* = 1 - 0.046$$

$$= 0.954$$

$$x_n^* = z_f - k$$

$$x_n^* = 0.9932 - 0.046$$

$$= 0.9473$$

$$c = 1 + (\alpha - 1)k$$

$$c = 1 + (2.2795 - 1)0.046$$

$$= 1.0588$$

$$\beta = {}^{sc(\alpha - 1)}/_{\alpha - sc^2}$$

$$\beta = {}^{0.9444 * 1.0588(2.2795 - 1)}/_{2.2795 - 0.9444 * 1.0588^2}$$

$$= 1.0482$$

Number of stages are:

$$N = \frac{\log\left[{}^{x_0^*(1 - \beta x_n^*)}/_{x_n^*(1 - \beta x_0^*)}\right]}{log\left({}^{\alpha}/_{sc^2}\right)}$$

$$N = 14.329$$

$$N \sim 15\ stages.$$

Stripping Section:

$$s = {}^{R * z_f + x_d - (R + 1)x_b}/_{(R + 1)(z_f - x_b)}$$

$$s = \ 1.0006$$

$$b = {}^{(z_f - x_d)x_b}/_{(R + 1)(z_f - x_b)}$$

$$b = -0.0001$$

$$s(\alpha - 1)k^2 + [s + b\ (\alpha - 1) - \ \alpha]k + b = 0$$

$$k = 0.9992$$

$$x_n^* = \ z_f - k$$

$$x_0^* = \ 0.9932 - 0.9992$$

$$= \ -0.006$$

$$x_n^* = x_b - k$$

$$x_n^* = 0.3248 - 0.9992$$

$$= -0.674$$

$$c = 1 + (\alpha - 1)k$$

$$c = 1 + (2.2795 - 1)0.9992$$

$$= 2.2785$$

$$\beta = {sc(\alpha - 1)}/{\alpha - sc^2}$$

$$\beta = {1.0006 * 2.2785(2.2795 - 1)}/{2.2795 - 1.0006 * 2.2785^2}$$

$$= -1.001$$

$$N = \frac{\log\left[{x_0^*(1 - \beta x_n^*)}/{x_n^*(1 - \beta x_0^*)}\right]}{log\left({\alpha}/{sc^2}\right)}$$

$$N = 7.095$$

$$N \sim 8\ stages.$$

$$Total\ number\ of\ stages = 15 + 8 = 23\ stages.$$

5.5.2 Plate Efficiency.

Plate efficiency assumed to be 70%.

$$Number\ of\ actual\ stages = \frac{23}{0.7}$$

$$N_{actual} = 33\ stages.$$

5.5.3 Column Diameter.

Plate spacing is estimated to be: 0.5 m

$$\widehat{u_v} = (-0.171 l_t^2 + 0.27 l_t - 0.047) * \left[{\rho_l - \rho_v}/{\rho_v}\right]^{1/2}$$

$$\widehat{u_v} = (-0.171 * 0.5^2 + 0.27 * 0.5 - 0.047) * \left[{882.39 - 1.84}/{1.84}\right]^{\frac{1}{2}}$$

$$= 2.86\ m/s$$

$$D_c = \sqrt{4\,\widehat{V_w} / \pi \rho_v \widehat{u_v}}$$

$$Vapour\ rate\ V_w = \frac{50000}{3600}$$

$$V_w = 13.89\ kg/s$$

Therefore:

$$D_c = 1.83\ m$$

5.5.4 Column Height.

Plate spacing is estimated to be: 0.5 m

Additional height due to condenser: 4 ft or 1.219 m

Additional height due to reboiler: 6 ft or 1.829 m

Therefore:

$$H = (33 * 0.5) + 1.219 + 1.829$$

$$H = 19.55\ m$$

5.5.5 Feed Point Location.

From rectifying section:

$$\frac{15}{15 + 8}$$

$$= 0.65$$

Feed point location:

$$Stage\ number = 33 * 0.65$$

$$N_{stage} = 21.45$$

$$N_{stage} = 22$$

5.6 Absorption Column.

5.6.1 Material balance.

$$Gm(y_1 - y_2) = Lm(x_1 - x_2)$$

where,

G_m = flow rate of gas entering (kgmoles/hr)

L_m = flow rate of solvent entering (kgmoles/ hr)

y_1 = mole fraction of CO_2 in entering gas stream

y_2 = mole fraction of CO_2 in leaving gas stream

x_1 = mole fraction of CO_2 in entering solvent stream

x_2 = mole fraction of CO_2 in leaving solvent stream

$$92262.1(Y - 0.0006) = 8152.0(X - 0)$$

$$X = 11.3710(Y - 0.0006) \ \dots \ (1)$$

$$Y = 0.0883X + 0.0006 \ \dots \ (2)$$

Equations (1) and (2) are the operating line equations.

5.6.2 Equation for equilibrium curve.

Let

Y1 = mole fraction of CO_2 in entering gas stream = 0.2380

Y2 = mole fraction of CO_2 in leaving gas stream = 0.0006

Y1/Y2 = 0.2380/0.0006 = 397

As

$$Gm\ (y_1 - y_2) = Lm(x_1 - x_2)$$

$$y_1 - y_2 = (Lm/Gm)(x_1 - x_2)$$

The above equation is in the form $y = mX + 0$

From Figure 11.40 in Coulson & Richardson Volume 6, we can find out the N_{OG} using Y1/Y2 & m G_m/L_m. Where 'm' is slope of equilibrium line.

Colburn has suggested that the economic range for m G_m/L_m lies from 0.7 to 0.8.

For our system, m = 0.07

G_m/L_m = 92262.1/8152.0 = 11.3710

m G_m/L_m = 0.79

From graph:

Area under the curve = N_{OG} = 37

5.6.3 Calculation of diameter of column.

Flow rate of entering gases = G = 92262 kg/hr

Flow rate of entering solvent = L = 8152 kg/hr

Temperature of entering gas = T_g = 226 °C

Temperature of entering Solvent = T_L = 473 °C

Pressure of entering gases = P = 30 bar

Average molecular weight of entering gases = 19

Density of gas mixture = $\boldsymbol{\rho g} \;=\; PM\;/RTg$

$$= \;(30 \times 19)/(0.08205 \times (226 + 273))$$

$$= 13.92\;kg/m3$$

Density of liquid solvent at 473 °C = $\boldsymbol{\rho_L}$ = 859 kg/m^3

Viscosity of liquid solvent at 473 °C = μ_L = 0.29 cP

Viscosity of Gaseous mixture at 226 °C = μ_g = 0.0184 cP

Now

Abscissa of Figure 11.44 in Coulson & Richardson Volume 6,

$$\frac{L}{G}\sqrt{\frac{\rho_g}{\rho_L}} = 0.012$$

For pressure drop 0.456 bar/m of packing

From Figure 11.44 in Coulson & Richardson Volume 6,

K_4 = 1.2

Also, from Table 22.1 in McCabe & Smith 5th Ed,

Packing factor for 1-inch plastic pall rings = Fp = 18

From Coulson & Richardson Volume 6,

$$G* = [k4 \times \rho g \times (\rho L - \rho g) / 13.1 \times Fp \times (\mu L / \rho L)\ 0.1]\ ½$$

$$G* = [1.2 \times 13.92 \times (859 - 13.92) / 13.1 \times 18 \times (0.29 \times 10 - 3 / 859) 0.1] 1/2$$

$$G* = 16.3\ kg/m2 - sec.$$

$$Flow\ rate\ of\ gas\ entering = G = 92262/3600 = 25.6\ kg/sec.$$

As

Area = $A = G / G* = 1.57\ m2$

Diameter of column: $D = 4[A]$ ½

[3.14] ^{½}

Thus, diameter of column = 2.83 m

5.6.4 Calculation of height of transfer units.

From Coulson & Richardson Volume 6,

Equation for calculation of effective interfacial area is given as:

$$\frac{a_w}{a} = 1 - \exp\left[-1.45\left(\frac{\sigma_c}{\sigma_l}\right)^{0.75}\left(\frac{L_w}{a\mu_L}\right)^{0.1}\left(\frac{L_w{}^2 a}{\rho_L{}^2 g}\right)^{-0.05}\left(\frac{L_w{}^2}{\rho_L \sigma_L a}\right)^{0.2}\right]$$

where

$aw = effective\ interfacial\ area\ of\ packing\ per\ unit\ volume\ m2/m3$

$Lw = liquid\ mass\ velocity\ kg/m2s$

$a = actual\ area\ of\ packing\ per\ unit\ volume\ m2/m3$

$\sigma c = critical\ surface\ tension\ for\ particular\ packing\ material$

$\sigma L = liquid\ surface\ tension\ N/m$

$a = 92\ m2/m3$

$Lw = 1.79\ kg/m2s$

$\sigma c = 75\ x\ 10 - 3\ N/m$

$\sigma L = 85\ x\ 10 - 3\ N/m$

$\mu L = 0.29\ cP$

$\rho L = 859\ kg\ /m3$

Substituting the values in the equation gives:

$$aw = 51.4\ m2/m3$$

5.6.5 Calculation of liquid film mass transfer coefficient.

$$K_L\left(\frac{\rho_L}{\mu_L g}\right)^{\frac{1}{3}} = 0.0051\left(\frac{L_w}{a_w\mu_L}\right)^{\frac{2}{3}}\left(\frac{\mu_L}{\rho_L D_L}\right)^{-\frac{1}{2}}\left(ad_p\right)^{0.4}$$

K_L = liquid film coefficient m/s

d_p = packing size = 40 x 10^{-3} m (From Table 11.4 Coulson & Richardson Volume 6)

D_L = diffusivity of liquid = 2.0 x 10^{-9} m^2/sec

Then, by substituting the values,

K_L = 7.38 x 10^{-4} m/s

5.6.6 Calculation of gas film mass transfer coefficient.

$$\frac{K_G RT_g}{aD_g} = K_5\left(\frac{V_w}{a\mu_g}\right)^{0.7}\left(\frac{\mu_g}{\rho_g D_g}\right)^{\frac{1}{3}}\left(ad_p\right)^{-2}$$

K_G = Gas film coefficient, kmol/m^2s.bar

V_W= Gas mass velocity = 92262/(3600x1.57)=16.3 Kg m^2/sec

K_5= 4.78 (For packing size above 15mm, Coulson & Richardson Volume 6)

D_g =Diffusivity of gas = 2.33 x 10^{-5} m^2/sec

Then, by substituting the values,

K_G =1.01 x 10^{-2} kmol/m^2s.bar

Now,

$$H_G=\frac{G_m}{K_G a_w P}$$

Where,

H_G = Gas-film transfer unit height

G_m = 16.3/19 = 0.86 Kmol/m^2.sec

Then,

$$HG = 0.86/\ (1.01\,x\,10-2\ \times\ 51.4\ \times 2.5)$$

$= 0.37\,m$

(From Coulson & Richardson Volume 6, Table 11.2, for plastic pall rings it is almost 0.40 m)

$$H_L = \frac{L_m}{K_L a_w C_t}$$

And

H_L= Liquid-film transfer unit height

L_m= 14.4/18 = 0.80 kmol/m^2.sec

C_t = Concentration of solvent = 859/18 = 47.7 kmol/m^3

Then,

$$HL = 0.80/(6.94 \times 10-4 \times 51.4 \times 47.7)$$
$$= 0.47\,m$$

5.6.7 Calculation of height of transfer units.

As,

$$H_{oG} = H_G + \frac{mG_m}{L_m} \times H_L$$

H_G = 0.37 m

H_L = 0.47 m

So,

$$Height\ of\ transfer\ units = HOG = 0.37 + 0.79 \times 0.47$$
$$HOG = 0.74\,m$$

(From Coulson & Richardson Volume 6, Topic 11.14.3, range is 0.6 to 1 m)

5.6.8 Calculation of height of tower.

$$Total\ height\ of\ packing = Z = NOG \times HOG$$
$$Z = 37 \times 0.74 = 27.4\,m$$

Allowances for liquid distribution = 1 m

Allowances for liquid Re-distribution = 1 m

$$Total\ height\ of\ tower = 27.4 + 1 + 1$$
$$Zt = 29.4\,m$$
$$Total\ height\ of\ tower = 29.4\,m$$

Chapter 6: Simulation.

The fluid package used in this simulation was the General NRTL property package employing the Virial vapour phase model as referred in the literature on model selection for the acetic acid system.

Kinetic reactions were configured for acetic acid from methanol and carbon monoxide, propanoic acid from ethanol and carbon monoxide, and the water shift gas reaction in addition to the by-product reactions.

Activation energies and Arrhenius constants were referred from literature. Process conditions were sourced from Monsanto Company patents. Convergence was achieved with material and energy imbalances of less than 0.1%.

By reviewing the courses of on research the methanol carbonylation in the field of kinetic studies, it was revealed that the lack of the adequate thermodynamic studies and sufficient precision in the study of the simultaneous effects of operation conditions (temperature and partial pressure) has only led to the determination of the apparent rate constant and not the inherent constant.

This study leads to an efficient and simultaneous estimation of the effects of pressure, temperature, and the thermodynamic restrictions on kinetic investigation of the homogeneously rhodium catalysed carbonylation process and the determination of its intrinsic rate constant.

It was found that the general NRTL-Virial model is identified as a proper fluid property package for carbonylation system. It was also concluded that the equality of the initial reaction mixture under the different operating conditions in the kinetic studies is a correct assumption.

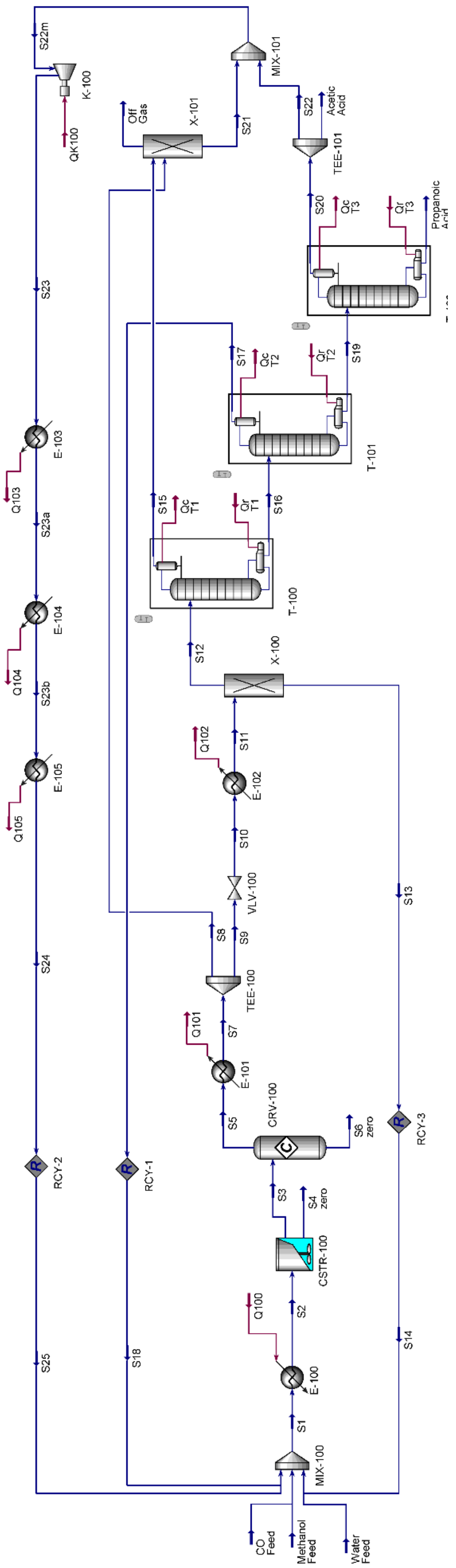

Figure 6.1: Simulation flowsheet from Aspen HYSYS V10

Chapter 7: Process Control and Instrumentation.

This chapter will describe the process control and instrumentation process employed in the Monsanto process to optimize it. The instrumentation ensures that the process remains safe for its user.

7.1 Introduction to Process Control and Instrumentation.

The premise of process control and instrumentation consists of applying the philosophies of control to all aspects of a process, whether that be the design of the process, the standard operation of the process or the operation of the process under conditions that vary from the norm, for example during a start up or shut down, as the only way to have a safe system, is to have reliable control systems in place at all times. As well as safety, putting in place reliable and effective control systems also aids in improving plant efficiency and the economic stability of the process while ensuring the plants compliance with the relevant environmental and safety regulations.

As the philosophies of process control and instrumentation are incorporated into every aspect of a process, the instrumentation that's implemented into a process should be integrated within the earliest design instead of being an afterthought that's 'bolted on' once the design has been completed. Implementing process control systems in this way will lead to the safety features of the process being much more effective with regards to plant safety and the safety of those in and around the plant, in addition to being much simpler because they have not been worked into the system, around an already complete process without the necessary control features put in place.

7.2 Objectives of Process Control.

The primary objective of the control systems and instrumentation put in place is to ensure that the process is carried out in a safe and reliable manner while producing a product that meets the required specification desired by the consumer. This can be achieved by:

1. Maintaining process variables within known safe operating limits around a specified set point.
2. Alerting operators to deviations from the set point and safe operating limits and provide a solution to the deviation either via the manipulation of process equipment or shutdown systems.
3. Preventing operators from altering process variables such that operation outside the safe operating limits is caused.

The four main process variables that have been controlled throughout the design stages of this project are:

1. Temperature.
2. Pressure.
3. Level.
4. Flow.

The variables have been controlled through the manipulation of various pieces of process equipment, such as control valves, via information sent to them through a series of indicators, alarms and controllers. The process equipment works to control any deviations from the desired set point, within an upper and lower limit. The control measures also have to accommodate for planned changes in the set point, for example, during start-up and shut down in which the desired set point for each of the process variables is going to vary from that of a steady state operation. This can be seen in the reactor, for example, during its start-up process, the set point would be at its desired operating conditions to ensure that the reaction took and a product was being produced. As the reaction continues and begins to reach a steady state the heat released by the reaction will cause an increase in the temperature of the reactor and therefore, a deviation from the desired operating conditions. In this case the set point can be decreased below the desired operating conditions while the heat released by the reaction can be used to maintain the required temperature. Variations in the set can be fine-tuned using the instrumentation in place to control situations like this.

In addition to process safety, operability has to be taken into consideration when implementing control features throughout the design stages of a project, as having too many indicators and alarms, etc., can reduce the operability of the process as having "too much data being thrown at operators reduces their ability to understand what is happening and respond correctly" (Hurley, 2016). This has been taken into consideration when implementing control features into the design of our process as it is possible to manage a combination of process variables by manipulating just one of them. Although this could lead to undesired variations in some of the process variables when manipulating others, therefore it is important to understand the relationships each of the process variables share with each other and what impact their variation would have on the process streams as well as the process equipment. An example of this can be seen in the transition of streams through a pressure reduction valve. The purpose of the valve is to reduce the streams pressure before it enters the flash tank, but as a consequence of reducing the pressure, the temperature of the stream is also reduced. The relationship between the two process variables is clear in this case, which would make it easier to identify the hazards a variation of pressure would cause downstream of the valve whether that be to the flash tank or other pieces of process equipment.

7.3 Implementation of Control Systems in our Design.

The types of control that have been taken advantage of throughout the design process of this project has been feedback, feedforward and cascade, with feedback and feedforward being the simpler forms of control and cascade being more complex. A feedback control system measures a process variable downstream of a piece of process equipment and then send information back upstream for the process equipment to manage the process variable directly. Similarly, to feedback control, feedforward control only measures and alters one process variable, although the process equipment is downstream of the measuring equipment instead of being the other way around in feedback. Whereas cascade control measures a process variable then alters another to result in a change to the original measured process variable.

Feedback control can be seen throughout the process P&ID, an example of the utilization of feedback control can be seen in the Figure 7.1. The figure shows a set of pumps in parallel with feedback-controlled valves based on the flow through the pipe. This has been implemented into the system with pump failure in mind, for example, if P-401 was the operational pump and P-402 was being used as a backup, both V-402 and V-404 would be closed to prevent any flow through P-402 under normal operating conditions. In the event of P-401 failing, V-403 and V-405 could be closed from the control room to prevent flow through P-401 while the pump was either replaced or having maintenance carried out on it. Valves V-402 and V-404 could then be opened from the control room and P-402 would become the operational pump in this system. The ability to switch between pumps because of the control systems in place would lead to much less downtime required in the event of the operational pump failing in comparison to a system without these control measures in place.

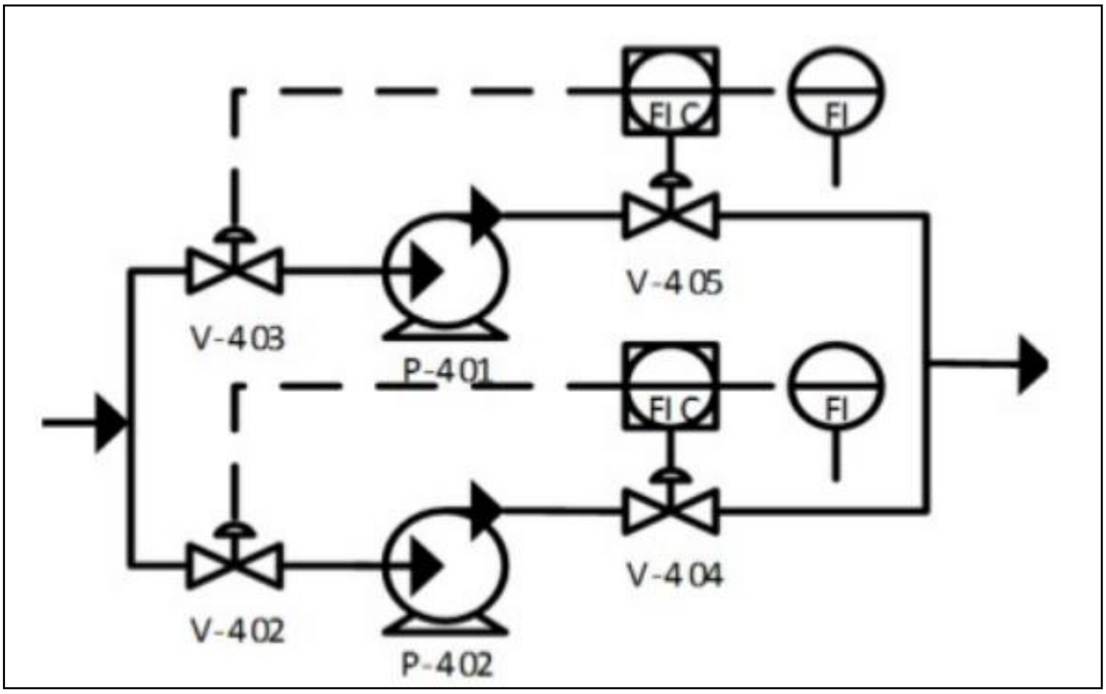

Figure 7.2: Pumps P-401 and P-402 are in parallel with flow control.

This type of control measure ensures that the operational time of the plant is not reduced due to pump failure and therefore maintains a high plant economic efficiency.

Cascade control can be seen in the instrumentation implemented around each of the distillation columns, more specifically around the condenser and reboiler. The temperature of the streams that are recycled from the condenser and reboiler will impair the columns performance if they are not as they should be, therefore it is important that the temperature is maintained in those streams. The cascade of control is used to control the temperature of the recycle streams by controlling the flow rate of cooling water and steam into the condenser and reboiler respectively. This system has been chosen as it is relatively easy to control the flow of cooling water and steam via the opening and closing of a valve when compared to directly controlling temperature.

7.4 Distillation column control.

Cascade control can be seen in the instrumentation implemented around each of the distillation columns, more specifically around the condenser and reboiler, as shown in Figure 7.2. The temperature of the streams that are recycled from the condenser and reboiler will impair the columns performance if they are not as they should be, therefore it is important that the temperature is maintained in those streams. The cascade of control is used to control the temperature of the recycle streams by controlling the flow rate of cooling water and steam into the condenser and reboiler respectively. This system has been chosen as it is relatively easy to control the flow of cooling water and steam via the opening and closing of a valve when compared to directly controlling temperature.

This system of cascade control also allows for effective pressure control when coupled with the ability to control the flowrate of the vapour stream. Effective pressure control can be achieved through controlling the flowrate of the vapour leaving the column, i.e. less vapour leaving the column will cause an increase in pressure throughout it. This flowrate of the vapour stream is controlled by the valves V- 308, V-408 and V-508 on the light ends, drying and heavy ends distillation columns respectively. Figure 2 shows V-308 on the light ends distillation column.

The temperature control element of the system, as previously described, through the control of the process water flowrate, allows the control of the vapour stream composition and importantly, gives an operator the ability to keep the stream composition constant.

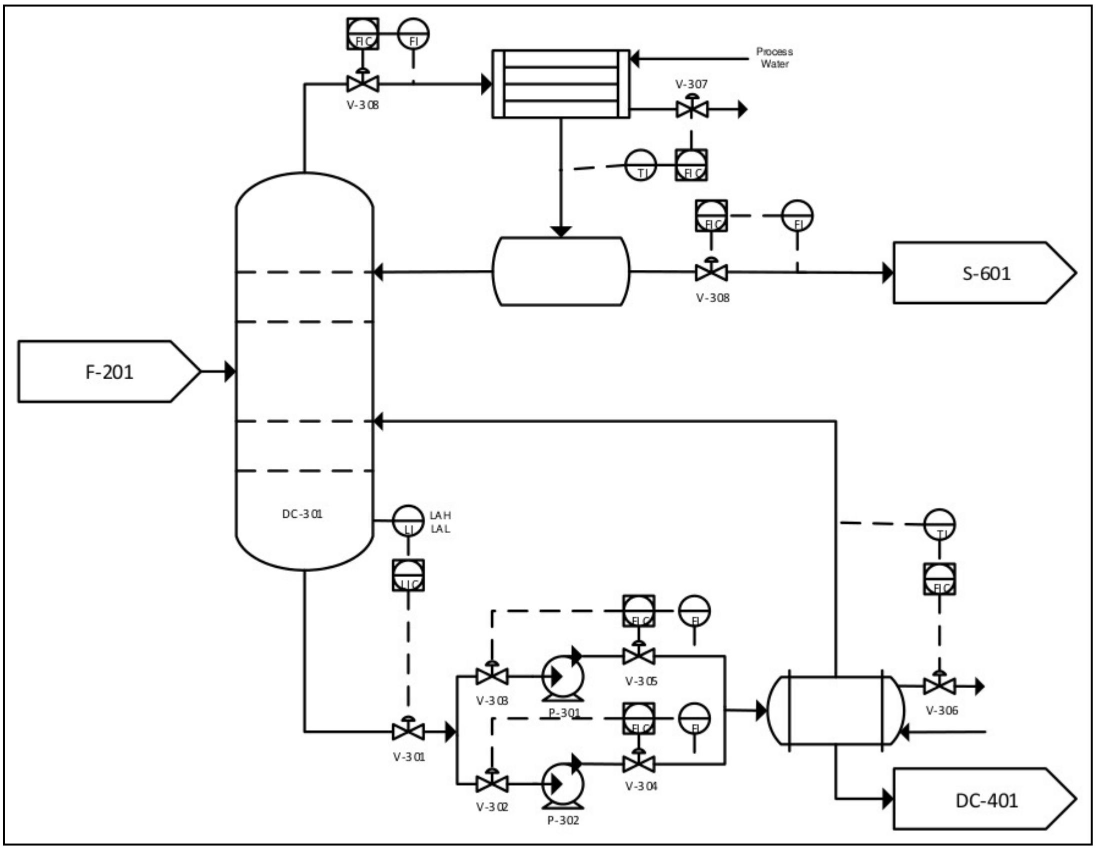

Figure 7.3: P&ID of DC-301 and control systems.

7.5 Reactor and Flash tank control.

Cascade control can also be seen on the system controlling the flow into, and out of, the flash tank and reactor respectively. Figure 7.3 describes the system around the reactor, R-201, and flash tank, F-201, as shown by the P&ID. The flowrate of the liquid leaving the reactor and therefore, entering the flash tank is controlled by the valve, V-201 which is in turn, is being controlled by the level in the reactor through the level instrumentation put in place. Similarly, for the flask tank, the liquid flow out of the flask tank, which is being recycled back into the reactor, is controlled by the valve, V-206 which in turn, is being controlled by the level in the flash tank through the level instrumentation put in place.

Valve V-203 is the pressure reduction valve required by the process, as it is a key piece of process equipment a backup valve, V-204, has been included for redundancy in the case of failure or in the event of maintenance being required on the operational valve. As V-203 is the valve used in normal operation, V-204 would usually be closed with V-202 and V-205 open to allow flow through V-203. Both valves V-202 and V-205 can be closed to isolate V-203 in the event of its failure and/or requirement for maintenance.

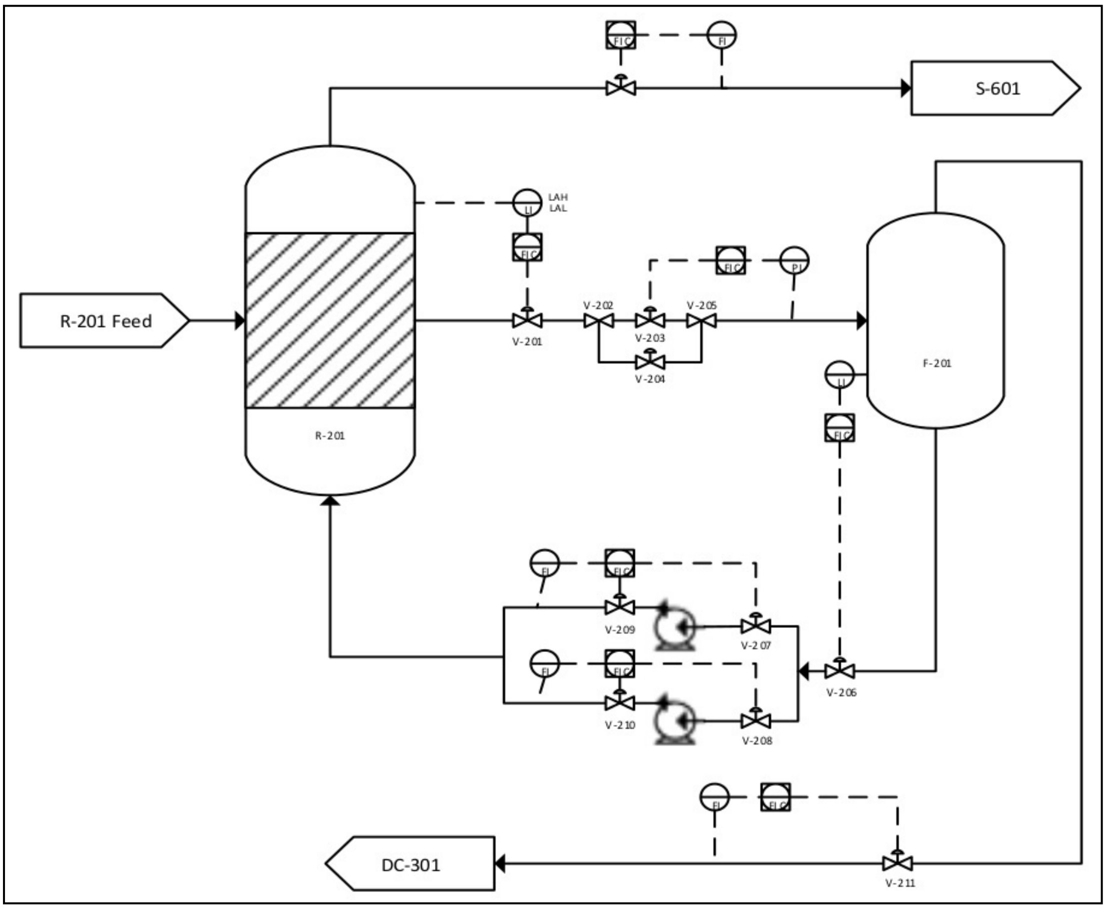

Figure 7.4: P&ID of R-201 and F-201 and control systems

Chapter 8: Economic Analysis.

This chapter will look in to an in-depth economic analysis of the process to ensure that the process developed is feasible.

The economic analysis is done in order to determine the feasibility of the process. Different forms of cost are incorporated in this analysis to get the overall cost of design. These costs include variable costs, capital costs, working capital and engineering costs etc.

Further, rate of investment and payback periods are calculated as well which depict the profitability of the process.

8.1 Market Analysis

In the current economic climate, demand for acetic acid is great and room for continuous growth is highly probable. (Grand View Research Inc., 2015) predict that "Global Acetic Acid Market is expected to reach USO 13.31 billion by 2022" as a result of products manufactured from acetic acid, such as Vinyl acetate monomer (VAM) extensively growing in demand. Henceforth, the development of an acetic acid plant will be very profitable in today's current market.

Acetic acid is a key precursor in the production of various commercial and industrial based products. Products range from households such as vinegar, a multifunctional household product used in cooking and as an ingredient in renowned sauces like ketchup, mayonnaise and mustard; additionally, it is also employed in cleaning products for the unclogging of drains and removal of lime scale deposits.

Although acetic acid is a key element in the manufacture of numerous commodities, the most significant product is Vinyl acetate monomer (VAM). The versatility of VAM allows for the production of various polymers such as polyvinyl acetate, polyvinyl alcohol, polyvinyl butyral and polyvinyl formal; these polymers are employed within industry as paint, adhesives and packaging. Literature on VAM reportedly states that the worldwide demand for the monomer back in 2003 was reported to be 4.3 million tonnes per year, contributing to 86% of overall acetic acid production worldwide. The maximum global production was approximately 5 million tonnes per annum, key contributors being Asia (43%), North America (34%} and Western Europe (18%) (Chemical Week, 2003). An additional source (Nexant, 2006), highlights data that reports global production of VAM reaching approximately 4.9 million per year in 2005. Furthermore, recent sources indicate further growth in VAM production (Merchant Research & Consulting Ltd, 2013) stating "2012, the overall VAM output climbed to around 6.5 million tonnes, registering growth of nearly 4% (259,000 tonnes)". As previously mentioned, there is significant evidence in support of the global demand for VAM, as a result of its thriving growth in industries such as construction, automotive, paints and coating. Continuous global growth in infrastructure at extreme rates leads to further expansion of VAM production.

Figure 1, illustrates pricing for VAM, Terephthalic acid (PTA) and Polyethylene terephthalate (PET) in 2013/2014. It can be noted that the pricing history of VAM does not fluctuate. VAM price predominantly remains constant, as further observation highlights the stable market price of just above 50 throughout 2013/2014. In comparison, the market price for other acetic acid commodities tend to be more fluctuating as observed by PTA, in which case a price spike is highlighted in November 2013 and an estimated 10% price increase in 2014.

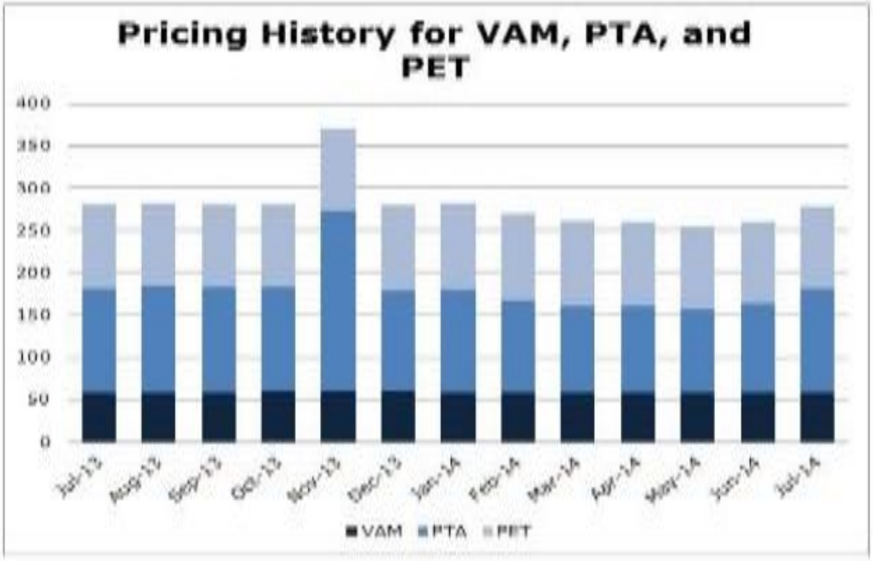

Figure 8.1: Graph showing the market pricing of the largest acetic acid products (Hicks, 2014)

Correspondingly, ester production also utilizes acetic acid to develop acetate esters, commonly used as solvents for inks, paints and coatings. Projected growth for cellulose acetate is encouraging as key drivers such as growing cigarette consumption in Asia makes it a market for exploitation. According to (Strategyr, 2016), drivers such as surface coating are fast growing and its respective market growth increasing by up to 4.1% CAGR. In addition, further reports project to exceed production of 951,000 tons by 2020 (Strategyr, 2016).

Acetic anhydride, another acetic acid-based product, is correspondingly doing well in the global market. IHS stated that "Global production of acetic anhydride has been growing at an average annual rate of 4% since 2007" (lhs, 2013). lhs also describes that acetic acid production in the United States, Western Europe and Japan declined at average annual rates of 3%, 2% and 4% respectively (lhs, 2013). Solvent glacial acetic acid is also due to witness major growth, as of right now the Asia-Pacific region is the biggest market of glacial acetic acid due to extensive growth in the automotive industry, especially China.

Each year, millions of tons of acetic acid is produced and exported globally. Numerous literatures have portrayed a market analysis of acetic acid, thus allowing to support the economic viability of acetic acid production. The key drivers for its demand are mentioned above, as well as projection of acetic acid market growth where major players such as British Petroleum PLC (BP) (UK), BP PETRONAS Acetyls Sdn Bhd (Malaysia), Celanese Corporation (USA), China Petroleum & Chemical Corporation (Sinopec Corp.) (China), Daicel Chemical Industries Limited (Japan), Kyodo Sakusan Co. Ltd. (Japan), DuPont (USA), Eastman Chemical Company (USA), Jilin Chemical Industrial Company Limited (China), Kuraray Co., Ltd. (Japan), LyondellBasell Industries (The Netherlands}, Millennium Chemicals Inc. (USA), Showa Denko K K (Japan), Sterling Chemicals Inc (USA) are facing tremendous benefits, thus it is possible to deduce that development of an acetic acid plant in this current market is viable and lucrative.

8.2 Costing

The basis for costing is to give an indication of process feasibility. Various costs are to be considered in order to provide a full financial evaluation of this design project. The following costs will be accounted for this study, being, feedstock costs, ISBL costs, OSBL costs, engineering costs, capital costs, working capital, plant component costs and servicing costs. In addition, this costing section will provide an indication of the fixed capital investment required for the project. Fixed capital investment considers the inside battery limits (ISBL) investment which portrays the cost of the plant and OSBL costs affiliated with construction, installation, commissioning and ground preparation.

8.2.1 Feedstock price estimation

The reaction for the Monsanto process is as follows:

$$CH_4O + CO \rightarrow C_2H_4O_2$$

Where, molecular weights are:

CH_4O = 32 kg/mol

CO = 28 kg/mol

$C_2H_4O_2$ = 60 kg/mol

The amount of methanol and carbon monoxide can then be derived through a stream analysis in Aspen. On the assumption that conversion is > 99%, 400,000 tons of acetic acid requires:

CO → 264794 tons per year

MeOH → 215488 tons per year

Water → 9312.55 tons per year

Table 20: Cost of Feedstock

Methanol required (t)	264794
Carbon Monoxide required (t)	245371
Rhodium iodide catalyst required (g)	5
Methanol cost per ton ($) (Chemical Market Reporter, 2006)	USD 330.00
Carbon Monoxide price per ton ($) (Soliman et al., 2012)	USD 50.00
Water required (tons) (Salisbury and Hallinan, 2015)	9312.55
Cost of water per ton (Quandl, 2014)	0.39
Rhodium price (per g)	22.53968
TOTAL METHANOL COST ($)	USD 87,382,020.00
TOTAL CARBON MONOXIDE COST ($)	USD 12,268,550.00
TOTAL RHODIUM CATALYST COST	USD 112.70
TOTAL COST OF WATER	USD 3631.89
TOTAL COST OF FEED	USD 99,654,314.89
Cost per ton of feed ($)	USD 195.34

8.2.3 Capital Cost Estimation

ISBL

To calculate the total ISBL costs, the Factorial method is applied, this will provide a class 4 estimated with an accuracy of 30%. Estimation are made based on the major items required for the process and other costs estimated as factors of the equipment cost.

Applying Lang Factors {Lang, 1948):

$$\mathrm{C} = \mathrm{F}\left(\sum C_e\right)$$

Where:

C = Total plant ISBL capital cost (including engineering costs)

$\sum C_e$ = Total delivered cost of all major equipment items

F = an installation factor (Lang Factor)

Thus, the cost of the major equipment is listed (corresponding cost include location and cost index for UK 2015 basis):

Table 21: Collated cost of equipment

Equipment	**Cost of Equipment, £**	**Material Factor**	**Ce (incl Material Factor, £**
Storage Tank	333,000.00	1.3	432900
Reactor	756,412.00	1.55	1200000
Flash Drum	66,225.95	1.55	103000
Light End column	542,826.88	1.55	840000
Drying Column	363,770.96	1.3	470000
Heavy End Column	145,002.00	1.3	189000
Scrubber	25,000.00	1.55	38750
$\sum \boldsymbol{C_e}$	**2,232,237.79**		**3,250,000**

INSTALLATION FACTOR

Installation factors then need to be accounted of, Table 6.3 contains a list of installation factors (Hand, 1958):

Table 22: Table of installation factors

Equipment Type	Installation Factor
Compressors	2.5
Distillation columns	4
Fired Heaters	2
Heat exchangers	3.5
Instruments	4
Miscellaneous Equipment	2.5
Pressure vessels	4
Pumps	4

Thus,

$$\mathrm{F}(\sum C_e) = £\ 82{,}500{,}000$$

OSBL

The off-side costs (OSBL) are accountable for infrastructure, which includes laboratories for technical staff, offices, canteens and various mandatory staffing facilities. Considerations of water treatment systems, security warehousing and loading facilities and maintenance costs are also included within the OSBL.

OSBL costs are estimated to be approximately 40% of the ISBL costs. Therefore:

OSBL costs= £33,000,000 (UK 2015)

ENGINEERING COSTS

Engineering costs are incurred by hiring contractors, costs acquired from the design, procurement of plant equipment, supervising construction and service installations. In addition, admin charges, insurance and contractors profit.

The cost of engineering is 20% of the sum of ISBL and OSBL costs for a large acetic acid plant. Therefore:

Engineering costs = £23,100,000 (UK 2015)

CONTINGENCY COSTS

The contingency cost are provisions for unexpected events that may cause financial consequences on the project such as labour disputes, price variations, FOREX Fluctuations, unforeseen weather conditions.

The contingency cost for this acetic acid plant is estimated at 15% due to the use of well-known technology. Therefore:

Contingency costs = £17,300,000

FIXED CAPITAL INVESTMENT

The capital cost for this project is the sum of ISBL, OSBL, Engineering costs and contingency costs. Therefore:

Capital cost = £156,000,000 (UK 2015)

WORKING CAPITAL

This accounts for operating expenses from the commencing of plant start-up and operations. For this project the working capital is 20% as product inventory is fairly large. Therefore:

Working Capital = £23,100,000

TOTAL INVESTMENT

The investment is total expense. It corresponds to the sum of fixed capital investment and working capital. Therefore:

Total investment = £179,000,000 (UK 2015)

OPERATING EXPENDITURE

OPEX for this process is assumed to be 40% of the FCI. Therefore:

OPEX = £62,000,000

REVENUE

The annual revenue generated from the sale of acetic, Table 23 illustrates the projected annual sales:

Table 23: Table showing annual sales of acetic acid

TOTAL COST OF FEED (£)	GBP 68,800,000
Selling price of acetic acid per lb ($)	USD 0.38
Selling price of acetic acid per ton ($)	USD 760.00
Total sale (revenue) ($)	USD 304,000,000.00
Total Sale (revenue) (£)	GBP 227,000,000 (Adapted to a temporal factor (1.06) and a location factor (1.02 for the UK)

GROSS PROFIT

The gross profit margin is given by:

Gross Pro fit = Revenue - Cost of Feed - OPEX

= £97,000,000

Therefore:

Gross Margin = 69.81%

The margin percentage gives a good indication of how profitable the process is going to be, correspondingly a percentage of 69.81% is very economically feasible for an acetic acid plant.

PAY BACK PERIOD

$$\text{Pay back period} = \frac{\text{total investment}}{\text{average annual cash flow}} = 2.75 \text{ years}$$

Where:

Total investment = £179,000,000

Average annual cash flow = £65,000,000

RETURN OF INVESTMENT

Another important parameter to be considered when evaluating the project is the Return of Investment (ROI). Therefore:

$$\mathrm{ROI} = \frac{\text{net annual profit}}{\text{total investment}} \times 100 = 53.9\%$$

Where:

Net annual profit = £97,000,000

Total investment = £179,000,000

8.3 Simulation economics

To evaluate the economics of the developed process the Aspen Process Economic Analyzer (APEA) in Aspen V10 is employed. The total annual cost, which is made of operating and fixed cost, in addition to cost indices that indicate the profitability of the process, were calculated. The pricing of the raw materials and the products were referred from economic reports and nominal averages taken. The 2.87 year of pay-out period indicates that the process is profitable and design of the plant and its equipment is viable. This concurs with the theoretical costing and validates the results.

Table 24: Results of Aspen Economic Analyzer

Total Capital Cost (USD)	**29,079,100.00**
Total Operating Cost (USD/Year)	132,880,000.00
Total Raw Materials Cost (USD/Year)	110,589,000.00
Total Product Sales (USD/Year)	208,210,000.00
Total Utilities Cost (USD/Year)	9,464,280.00
Desired Rate of Return (Percent/Year)	20.00
Payout Period (Year)	2.87
Equipment Cost (USD)	9,213,700.00
Total Installed Cost (USD)	16,007,500.00

Chapter 9: Hazop Study.

This chapter will describe the possible hazards that can take place when the Monsanto process is functional on a plant. The Hazop study carries out a detail risk assessment of what hazards might occur when a process is fully functional.

Hazard and operability study analysis (HAZOP) is a qualitative technique, done to determine the potential hazard of equipment. HAZOP is done on both on and off-site equipment. The main aim of the HAZOP is to identify the hazardous situations and to determine the efficient working of the safeguards to prevent unwanted scenarios or to control those scenarios.

HAZOP is important to operate the plant within safe limits. We have developed the HAZOP for different nodes which would explain the methodology. HAZOP is necessary before building a chemical plant. In other words, it’s a legal requirement to quantify all the hazards and risk present on the plant.

9.1 Course of action

In the HAZOP analysis, the most important parameter is to select the critical nodes. We have selected the inlet of reactor as our first node since it’s the most critical one due to high pressure and temperature variables and the second node selected is the inlet of the light distillation column.

Before conducting the HAZOP, our group reviewed all the critical parameters and piping and instrumentation diagrams including equipment.

The parameters included in the study are:

- Flow
- Temperature
- Pressure

And the Guide words selected are:

- None
- More
- Less

These guide words were applied to each parameter and the deviation of each parameter from their intention, possible causes and consequences were studied. The team devised the recommendation plan as well to cater those deviations in future.

9.1.1 Study Node: Reactor inlet.

Table 25 Hazop Study at Reactor inlet.

Guide Word	Parameter	Deviation	Possible causes	Consequences	Action Required
No	Flow	No flow to Reactor	Blockage	No product formation	Installation of flow control btw reactor and flash tank
No		No flow to reactor	Pipe failure		Maintenance of plant piping
More		Excess flow to reactor	Greater fluid Density	Damage to valves	Inspection of valves
More		Excess flow to reactor	Control faults	flooding	Installation of flow control btw reactor and flash tank
Less		Less flow to reactor	Leakage in pipe	Product yield decreases	Installation level control valves
		Less flow to reactor	Valve partially open	Formation of side products	
More		High pressure of inlet stream	Malfunctioning of valve	Explosion of reactor	Installation of pressure relief valve

More	Pressure	High pressure of inlet stream	Control faults	Release of toxic material	Installation of rupture disc on reactor
Less		Low pressure of inlet stream Low pressure of inlet stream	Malfunctioning of valve Control faults	Decrease in catalytic activity Decrease in conversion	Pressure relief valve installation Using differential pressure control to ensure safe limit
More	Temperature	High temperature of inlet stream	Fire situation Failure of pressure reduction valve	Increased temperature in reactor leading to excess heat Damage to equipment Explosion	Ensure there is adequate warning of high temperature Pressure relief valves
Less		Low temperature of inlet stream	Low temperature in reactor	Incomplete conversion	Installation of temperature controls

9.1.2 Study Node: Lights Distillation Column Inlet.

Table 26 Hazop Study at Distillation Column inlet.

Guide Word	Parameter	Deviation	Possible causes	Consequences	Action Required
No	Flow	No flow to the column	Blockage	Distillation would not occur	Installation of flow control btw flash tank and lights distillation column.
No		No flow to column	Pipe failure		Maintenance of plant piping
More		Excess flow to the column	Greater fluid Density	Damage to the packing and vessel	Inspection of valves
More		Excess flow to column	Control faults	flooding	Installation of flow control btw flash tank and column
Less		Less flow to column	Leakage in pipe	Top and Bottom Products yield decreases	Installation level control valves
		Less flow to column	Valve partially open		

More	Pressure	High pressure of inlet stream	Malfunctioning of valve	Explosion of column	Installation of pressure relief valve
More		High pressure of inlet stream	Control faults	Direct effect on the volatility hence on separation	Installation of rupture disc on column
Less		Low pressure of inlet stream	Malfunctioning of valve	Direct effect on the volatility hence on separation	Pressure relief valve installation
		Low pressure of inlet stream	Control faults		Using differential pressure control to ensure safe limit

More	Temperature	High temperature of inlet stream	Fire situation Failure of pressure reduction valve	Increased temperature in the column would lead to separate both the top and bottom components as vapors Damage to equipment Explosion	Ensure there is adequate warning of high temperature Pressure relief valves
Less		Low temperature of inlet stream	Low temperature in reactor	Increased temperature in the column would lead to separate both the top and bottom components as vapours	Installation of temperature controls

9.2 Safety Conclusions.

After considering all the hazardous aspects present in the plant, we have developed this HAZOP study. Our report portrays the effective way of producing high quality and up to customer’s demand level of acetic acid while ensuring the safety limits.

While putting the nature of hazardous components and process conditions into account, its necessary to apply all the safety considerations for the safety of all the people on site.

Lastly, safety is an important feature of the design and its everyone’s responsibility to work for the safe environment since safe environment is a joint effort and must be regarded in the industry.

Chapter 10: Conclusion.

An eco-friendly engineering strategy has been applied to this project when dealing with significant by-products. Although the generation of highly corrosive chemicals (such as methyl-iodide) has not been possible to be prevent, other "waste" compounds produced in the system have been proved to be commercially useful (propionic acid). Certainly, a comprehensive recycling system within the plant (and especially to the reactor) is a successful strategy to ensure that non desired products are dealt with the purpose of minimizing waste. Furthermore, even when waste streams are unable to be recycled and re- used in the system, appropriate techniques to dispose of them have been developed in compliance with environmental regulations and ethical considerations i.e. flares, aqueous discharge basin and pipeline.

Careful consideration of all the hazards present on the plant are outlined in the following report which highlights efficient ways of maintaining a safe environment for the production of acetic acid.

In addition to environmental methodologies, principles of process control and instrumentation have been applied throughout the design stage of this project with the aim of creating a process that is ultimately safe, that complies with all the necessary safety regulations, efficient, that will not suffer unnecessary downtime to avoidable failures and maintenance being carried out on key piece of process equipment and not suffer performance impairments due to poor design, as well as being economically stable, linked to the plants efficiency, an efficient plant will bring a certain amount of economic stability in addition to ensuring unnecessary equipment or instrumentation is not put in place.

Based on market research it is possible to conclude that the acetic acid market is projected to rise the upcoming years on a global basis. Economic evaluation of this project indicates viability, the return of investment is 53% and the net profit of £1,378,000,000 is very lucrative figure for a 20-year investment. Both a bank loan and private equity investments would generate a greatly positive profit, although a bank loan would represent a significantly more profitable route. The project payback time of 2 years demonstrates that this project is highly feasible and has the potential to attract numerous investors.

The developed process has a production capacity of 1200 ton of acetic acid per day from the feedstock of methanol and carbon monoxide. Chemical process principles, thermodynamics, process design and simulation principles were applied throughout the design of this process.

As a result, the process is evaluated for a pay-out period of only 2.87 years which implies economic profitability and viability. The results of the simulation and the theoretical study concur to validify the design and calculations.

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