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PRODUCTION OF PHENOL

(Student F. name, L.name, Email)

ASPEN Plus Process Simulation

For ASPEN simulations of the phenol production process, we will use a zeolite catalyst. The material dissociates into ion during the process and hence dissolves. The EPNRTL property method was employed in the implementation of the simulation throughout the report.

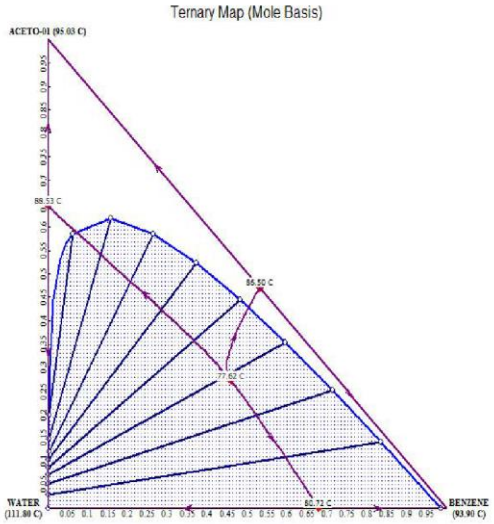
Assumptions

1. Catalyst Solubility

The zeolite catalyst used was not well defined. Hence, there was the need to make meaningful assumptions. This is because the solubility of the catalyst will influence the separation section of the process i.e. can result in clogging of the pipe and the distillation column trays. From the IUPAC analysis, most of the catalysts parts were soluble.

2. Acetone Minimization

Assumptions had to be made in regards with the solvent required for the process. From the analysis of water, acetone and the benzene mixtures in the reactor, it was necessary to maintain the miscible single-phase solution at 22 psi.



Ternary Map of Water/Acetone/Benzene at 22 psi & 140 F

3. **Hydrogen peroxide Quality**

Commercially obtained hydrogen peroxide have additives to enhance their stability. The quantity of the stabilizers will always increase with the increase in the strength of the hydrogen peroxide. The analysis assumes that the hydrogen peroxide does not contain stabilizers so as to avoid them being present in the system.

4. Waste Treatment

The project will assume that waste treatment already does exist or will be included due to the nature of the chemical processes carried out.

Simulation in ASPEN plus

Discussion

The reactor is where the primary process of propylene and benzene react hence has to be modeled as specified in the components list. The alkylation and trans-alkylation reactors

are modeled separately. A temperature range of 300-400 oC and pressure of 25 atm are adopted.
Using the equilibrium condition pressure is not considered as the reaction occurs at equilibrium pressure but is dependent on temperature and the benzene/propylene ratio. ASPEN Plus has seven reactor models available. The equilibrium dependent RGIBBS reactor is executed in fathoming the constituents of the substance where free enthalpy of the product is at its lowset

The temperature approach for each reaction is implemented while the feed stream mole flow rate is maintained at a value of one kmol/hr and the feed stream comprises of propylene and benzene. The temperature of the reactor is set at 350 oC and pressure at 25 atm. The effects of variation of temperature and the selectivity in the conversions are monitored.

The calculations made are based on the following formula
%Selectivity of cumene = Fcumeneproduct /(Fpropylenefeed-Fpropyleneprod) x 100%

%Conversion of propylene = (FpropylenefeedFpropyleneprod)/Fpropylenefeed x 100 %

%Selectivity of *m*-DIPB = Fmdipbproduct/(Fpropylenefeed-Fpropyleneprod) x 100%

%Selectivity of *p*-DIPB = Fpdipbproduct/(Fpropylenefeed-Fpropyleneprod) x 100%

Where
Fcumeneproduct = molar flow rate of cumene in product

Fpropylenefeed = molar flow rate of propylene in feed

Fpropyleneprod = molar flow rate of propylene in product

Fmdipbproduct = molar flow rate of *m*-DIPB in product

Fpdipbproduct = molar flow rate of *p*-DIPB in substance.

RSTOIC reactor models was adapted in finding the standard heat of reaction for the various reactions

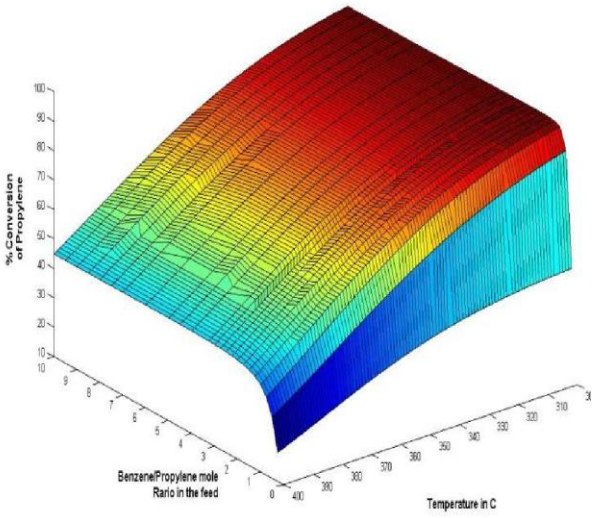
Reaction Number	Standard Heat of Reaction (Kcal/Kg mol)
1	-23.670
2	-24.321
3	0
4	0.649
5	0.649
6	-0.325
7	-0.324

Impact of temperature and benzene/propylene concentration on the reaction.

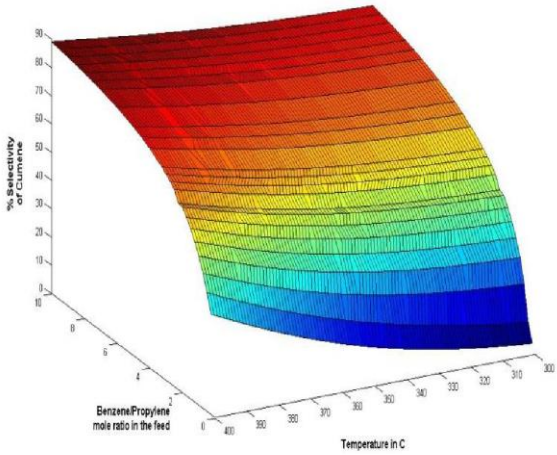
The conversion of propylene increased with addition of the benzene/propylene concentration for a given temperature. This is due to the reduced proportion of propylene in the feed. The conversion of propylene was found to be decreasing with every addition of heat applied for a constant benzene/propylene concentration as a result of the reaction being exothermic. Finally, the selectivity of Cumene increased with each rise in benzene/propylene concentration at a given temperature as the polyalkylation reactions become reduced due to the excess amount of benzene. The increase in temperature increases the selectivity of Cumene for any static benzene/propylene concentration like

trans-alkylation reactions being endothermic occur at high temperatures.

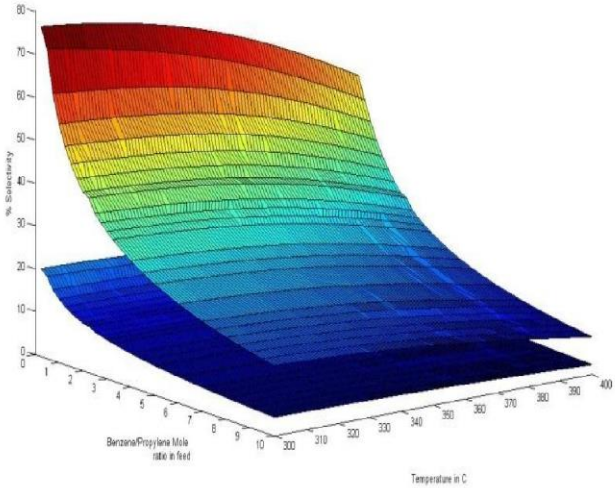
a) Impact of increase/decrease in temperature and benzene:propylene concentration on conversion of propylene.



b) Impact of increase/decrease in temperature and benzene:propylene concentration on selectivity of cumene



c) Impact of increase/decrease in temperature and benzene:propylene concentration on selectivity of *m*-DIPB and *p*-DIPB.



This process of phenol production involves purified or recycled cumene being oxidized. Cumene is fed in a stream into the oxidation vessel which is maintained at 110-115 ^{o}C and pH range of 6.0 to 8.0. This mixture is maintained exposed to compressed air until at least 20-25% of the cumene is converted to cumene hydroperoxide

$$C_6H5CH(CH_3)_2 + O_2 \Longrightarrow C_6H_5C(CH_3)_2OOH$$

This crude mixture is concentrated to 80% then injected to a reactor where the Cumene hydroperoxide is cleavage to phenol and acetone at around 70 ^{o}C and the atmospheric pressure. The reaction requires a small amount of Sulphuric acid so as to take place.

$C_6H_5C(CH_3)_2OOH \Longrightarrow C_6H_5OH + CH_3COCH_3$

The stream is then directed to the separation process, but first, it is washed in water, and the acetone is removed as the overhead in the first column. The mixture is then purified by successive distillation. In the first column, the unreacted Cumene is transferred to the recycle stream. This cumene is treated before sending it back to the feed stream.

The purification process is through catalytic hydrogenation of Methyl Styrene to cumene; this achieved through careful fractionation where methyl styrene is obtained as a by-product.

The reaction of phenol was in two steps. The first reaction is the production of Cumene hydroperoxide by two raw materials i.e. cumene and oxygen. The reaction takes place in the oxidizing tower at 110-115 oC and pH range of 6.0 to 8.0. The intermediate product which is cumene hydroperoxide is used as a reactant in the second reactor, the reactor intended to be used is the Continuous Stirred Tank Reactor (CSTR). Most of the conversion occurs here i.e. about 90%. In the separation process, the side product and waste are removed to get the primary product i.e. Phenol.

Basic Process Flow Diagram and background

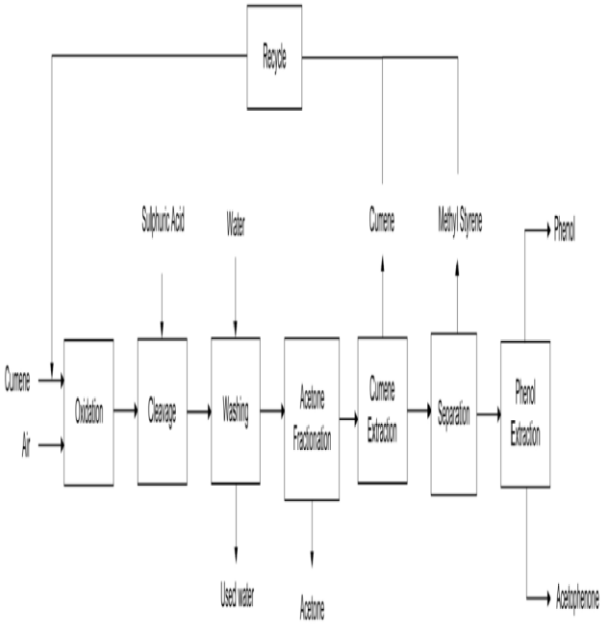
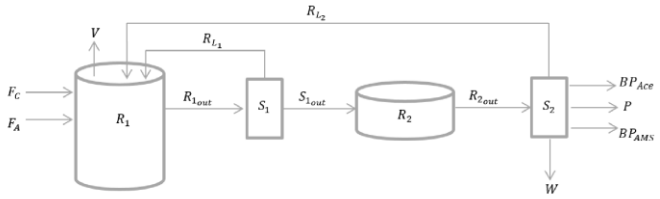


Figure 5: Block diagram for the process of Phenol



So as to do a simulation the phenol production process is composed of two processes i.e. oxidation and cleavage of Cumene

Hock process (oxidation of cumene)

$C_6H_5CH(CH_3)_2 + O_2 \quad C_6H_5C(CH_3)_2OOH$

$C_6H_5CH(CH_3)_2 + 1.5O_2 \rightarrow (CH_3)_2C_6H_3CH_2OH$

Cleavage reaction

$(CH_3)_2C_6H_3CH_2OH \rightarrow C_6H_4(C_2H_3)CH_3 + H_2O$

$C_6H_5C(CH_3)_2OOH \rightarrow C_6H_5OH + CH_3COCH_3$

Aspen process flow diagram

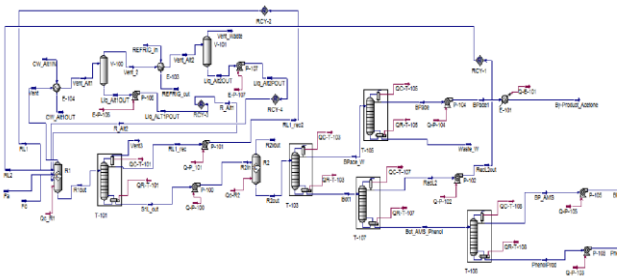


Table of distillate at various stages

Distillate flow rate kmol/hr	Benzene flow rate top product kmol/hr	Cumene flow rate top product kmol/hr	Benzene flow rate bottom product kmol/hr	Cumene flow rate bottom product kmol/hr
10	9.99929576	0.00070424	8.95256924	7.893145
14.4916664	14.49071	0.00095639	4.46115496	7.892893
16	15.9989608	0.00103922	2.95290423	7.89281
18	17.9988608	0.00113924	0.95300427	7.89271
20	18.9518649	1.04812842	8.41E-08	6.845721
22	1.90E+01	3.04806548	1.66E-08	4.845784

From the diagram the process has six steps

1. Oxidation of Cumene to obtain hydroperoxide
2. Cumene hydroperoxide concentration
3. Cleavage(decomposition of Cumene hydroperoxide)
4. Effluent neutralization
5. Purification
6. Effluent treatment

ASPEN plus report

ASPEN values

ASPEN PLUS PLAT: WIN32 VER: 25.0 05/16/2014 PA

COMPONENT SPLIT FRACTIONS ***
OUTLET STREAMS
S-310 S-304 S-301

COMPONENT:			
BENZENE	.21152E-01	.77888	.19997
PHENOL	.15733E-04	.24208E-01	.97578
WATER	.17077E-01	.97608	.68445E-02
ACETO-01	.37379E-02	.35571	.64056
OXYGEN	.50460	.49540	0.0000

ZINC--01 0 .0000 0.0000 1.0000

STAGE	TEMPERATURE F	PRESSURE PSIA	BTU/LBMOL LIQUID	VAPOR	HEAT DUTY BTU/HR
1	278.28	169.00	-26512.	-12939.	-.65506+08
2	321.81	169.00	-6544.5	-13913.	
3	319.04	169.00	-9457.1	-13881.	
4	322.52	169.00	-8617.9	-13026.	
17	353.28	169.00	19532.	29428.	
18	355.99	169.00	20418.	31243.	
19	358.38	169.00	20884.	32420.	
20	370.76	169.00	16026.	33262.	.10388+09

STAGE	FLOW RATE LBMOL/HR LIQUID	VAPOR	FEED RATE LBMOL/HR LIQUID	VAPOR	MIXED	PRODUCT RATE LBMOL/HR LIQUID	VAPOR
1	5208.	115.0				5207.9120	115.0317
2	22.62	5323.					
3	0.1339E+05	5346.	.10543+05				
4	0.1355E+05	8165.					

BLOCK: D-301 MODEL: RADFRAC (CONTINUED)
**** MOLE-X-PROFILE ****

STAGE	BENZENE	PHENOL	WATER	ACETO-01	OXYGEN
1	0.17300	0.32361E-02	0.35952	0.45807	0.61690E-02
2	0.12187	0.45222E-01	0.20132	0.63143	0.15172E-03
3	0.12260	0.52844E-01	0.21694	0.60715	0.43041E-03
4	0.12163	0.52289E-01	0.21218	0.61384	0.24346E-04
17	0.86600E-01	0.50232E-01	0.19567E-01	0.84357	0.0000
18	0.78864E-01	0.51658E-01	0.12816E-01	0.85664	0.85643E-21
19	0.70478E-01	0.54485E-01	0.81435E-02	0.86687	0.42192E-21
20	0.44314E-01	0.13014	0.25152E-02	0.82296	0.0000

Equipment to be purchased

1. Pump (p-201)
   To increase the pressure of benzene feed to 3000 kPa

2. Pump (p-202)
   To increase the pressure of propylene feed to 3000 kPa

3. Heater
   Vaporizes and superheats the mixture of the feed to 350 oC

4. Reactor

Where the conversion of the limiting reactants take place.

$$\underset{\text{propylene}}{C_3H_6} + \underset{\text{benzene}}{C_6H_6} \rightarrow \underset{\text{cumene}}{C_9H_{12}}$$

5. Flash vessel

The combination of the heat exchanger and a flash drum. Aimed at lowering the temperature and pressure to separate inert propane and unreacted propylene from the Cumene and benzene.

Hand calculation of reactants in the reactor.

Material and Energy Balance

The reaction in the first reactor shows that the one kmole of $C_6H_5CH(CH_3)_2$ and one kmole of O2 will produce one kmole of $C_6H_5C(CH_3)_2OOH$. Also in the presence of Sulphuric acid (H_2SO_4), one kmole of $C_6H_5C(CH_3)_2OOH$ will cleavage one kmole of C_6H_5OH and one kmole of CH_3COCH_3. Using the following standard relationship we can calculate the masses involved in the production of phenol.

Rate of mass input = Rate of mass output

Phenol production in a year
=136363.64 tonnes / year
= 15.56663 tonnes / h

= 15566.63 kg / h

= 165.6 kmole / h

Fraction of composition of the product in the cumene hydro peroxide in the mixture in the first reactor

X3cumene = 0.6
X3cumene hydro peroxide = 0.3
X3oxygen = 0.1
Conversion factor:
X reactor 2 = 90%

To obtain the molar rate in reactor 1 we first calculate the

Molecule Balance on reactor 2 (acidifier).

Phenol Balance:
N3X3phenol = N4X4phenol – ar2
N4X4phenol
=> 165.6 kmole / h
a = 1
0 = N4X4phenol – r2 **r2**
= 165.6 Kmole / h

Acetone Balance:
N3X3acetone = N4X4acetone–ar2
N4X4acetone = 165.6 kmole / h
Cumene Peroxide Balance:

N3X3cumene hydro peroxide= -ar2 / Xreactor2
= - (-1) (165.6) / (0.9)
= 184 kmole / h

Total number of mole in feed reactor 2, N3

N3X3cumene hydro peroxide= 184 kmole / h
X3cumene hydro peroxide= 0.3 N3 (0.3) = 184 kmole / h
N3 = 613.3 kmole / h

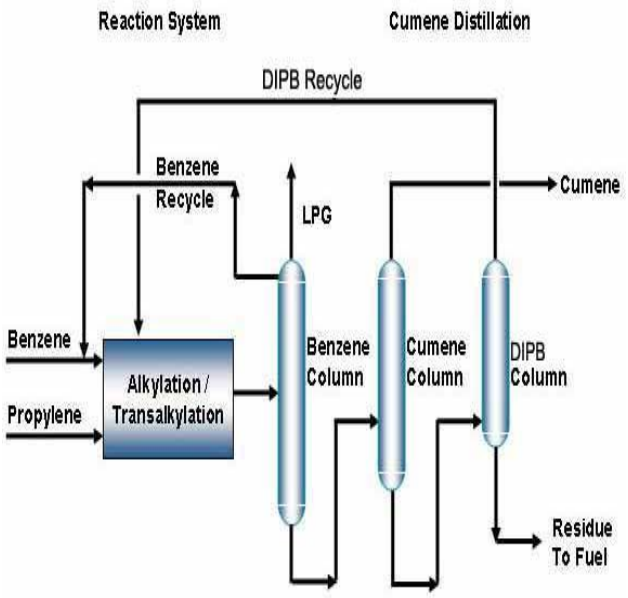
<u>Finding mass flow rate for feed in reactor 2.</u>

F3 = N3X3cumene (Mr_{cumene}) + N3X3 cumene hydro peroxide ($Mr_{cumene\ hydro\ peroxide}$) + N3X3oxygen ($Mr_{oxygen}$)

=> (613.33) (0.6) (120) + (613.33) (0.3) (150) + (613.33) (0.1) (32) = **73722.26 kg / h**

The values obtained indicate that reactor 2 would require 73722.26 kg/h of the Cumene hydro peroxide and Cumene and oxygen to produce 15566.63kg/h of phenol at the conversion rate of 90%.

To fully perform the material and energy balance in the system (hysys) there is a need to draw the conversion chambers and their respective input and output streams.



Comparison of the ASPEN plus results and the hand calculation results

From the data provide in the ASPEN plus report we can conclude that the hand calculation give a clear indication of the substance to be used. The simulation provides an ideal condition of the project.

Expected Input and Output

The primary goal of the design process is to analyze the cost and the fundamentals of production of 100000 metric tons of carbolic acid annually. From the chemical books, the molecular weight of Cumene is 120.20 g mol-1 and it has density of 862 kg/m^3. While Benzene has a density of 876 kg/m^3 and molecular weight of 78.11 g/mol. Finally Propylene possess a density of 1.81kg/m^3 and a molecular weight of 42.08g/mol. Conclusively Phenol has a density of 1070kg/m^3 while its molar mass is 94.11g/mol [9]. Putting these densities and molar masses in mind, the following input requirements are going to be made necessary: 255050 metric tons of Cumene, 728545 tonnes of propylene and 392490 tonnes of benzene to fabricate. These values are estimated to the closest five metric tons.

Economic Costs Analysis

In evaluating the alternatives, we do the profitability analysis based on the numbers of economic criteria i.e. payback period, cash flow analysis and internal rate of return. We apply the equivalent annual operating cost in the analysis

Profitability analysis

EAOC = -(product value - feed cost - other operating costs - capital cost annuity)

When the value of EAOC is negative, it indicates profitability. The cost of Cumene nad benzene was obtained from chemical marketing reporter. Capital cost annuity (an annual cost) is a one-time fixed cost that majorly entail the construction of the plant. It is defined as

$$capital\ cost\ annuity = FCI\ \frac{i(1+i)^n}{(1+i)^n - 1}$$

Where

FCI is the installed cost of all equipment;

i is the interest rate, $i = 0.15$;

n is the plant life for accounting purposes, *n* = 10.

Profitability discussion

For industrial application, the plan can be approximated to consume $ 25 million in fixed costs plus $ 127.6 million/year in direct capital expenditure [7]. The static costs will be accrued through the purchase of equipment such as; boilers, a pre-heater, a reactor, a heater, coolers, refluxes, a compressor, condensers, columns and condacuums [7]. Most of the direct capital costs will result from the purchase of raw materials. Which can be projected to cost of $1.37, $1.12, $1.20 and $3.30 per kg respectively for Cumene, propylene, benzene, and DIPB the basic materials are predicted to cause an annual expenditure of $ 133419932 $ 45552468, $ 79919133, and $12521737 in verbatim as tabulated below.

Raw material	Cost per kg ($)	Annual cost ($)
Cumene	1.37	133419932
Propylene	1.12	45552468
benzene	1.20	79919133
DIPB	3.30	12521737

Production Targets

Land Building and Machinery

Description	Measurement/ quantity	Cost
Covered area	Sq. Ft.	500
Uncovered area	Sq. Ft.	500
Total area	Sq. Ft.	1000
Rented premises		2000
Reactors	1	34255.03
Mixers	1	
Separation machines	1	

Estimated Cost Per Annum

Total recurring cost per year	26951.26
Depreciation on machinery and equipment	372.34
Interest on total investment @ 10%	595.74
total	27919.34

Sales

Item	Quantity	Value ($)
Phenol	100,000	34255.03
Total		34255.03

Profitability

Annual gross profit	6335.69
Percentage of profit on sales	18.50%
Annual fixed cost	8668.01
Annual sale	34255.03
Annual variable cost	18283.25
Break-even point	54.27%

Safety issues and hazard

Health and Safety

The need for safety management is rendered necessary by the presence of flammable and toxic materials. The process should consider control of process quality and deviations within the processes.

Process Safety Documentation

Benzene

This chemical is very hazardous when inhaled. It is also irritant to both skin and

eyes. When spilled to a great amount it should be prevented from coming into contact with heat or an ignition source. Protection gear should be worn like splash goggles, lab coats, and gloves. It is also considered to be carcinogenic.

Hydrogen peroxide

It has a skin and eye irritation effect. It is also corrosive to skin and eye in case of contact. It can also cause tissue and respiratory tract damage. Can cause combustion and provide oxygen to sustain fires. Personal protection equipment i.e. gloves, face shield, boots, vapor respirator and full suit should be worn.

Phenol

It is hazardous in case of contact or inhalation. It is irritating both to the skin and the eye. Exposure can also lead to lung, kidney, and central nervous system damage. Personal protection should include a synthetic apron, vapor, splash goggles, gloves and dust respirators.

Flammability Limits

Benzene has a flammability limit of 1.2 percent to 11.5 percent by volume in oxygen. Benzene being present in effluent vapor requires control mechanism to avoid fires. A controlled natural gas feed into the

Hazop analysis

The process of phenol production is exothermic hence there is provision for a cooling system. Interruption in the cooling system increases the temperature of the reactors. This changes in temperature can result into a runaway reaction that can ultimately rapture the vessels. The noted points of interest are the cooling water line, the monomer feed line, reactor vessel and the stirring motor. From the Hazop analysis we can get the following modifications:

1. Introduction of a high temperature monitoring system to alert operators
2. Installation of a cooling water meter and alarm for immediate indication in loss of cooling water.
3. Provision for a high temperature shutdown, which will shut the system in the event of reactor overheating.
4. Installation of a check valve to prevent reverse flow of the cooling water.

The Hazop report can be presented as:

System No:	System name:		Page of		
Report of Hazop study	Client:	Project	Content No:		
date	present		Report by:		
System number	System:				
No	Guide word	Deviation	Possible cause	Possible consequence	Action required
1A	Cooling coils	No	1. Unplugged Failed check valves 2. Plugged cooling coils	3. Loss of cooling ability of the system 4. Runaway	4. Installation of a fail valve 5. Provide filters for maintenance
2A	Stirring motor	No	1. Malfunction of the stirring motor 2. Power failure	1. No mixing of reactants 2. Accumulation of unreacted material 3.	1. Fail monomer feed valves.

Environmental Issues

Several production elements must be considered to make the plant environmentally friendly. Flare should be included to prevent organic compounds being released into the air. Any resulting gas effluents are combined, purified and passed through the flare for filtering of organic compounds. Methane is included as a

controlled feed to reduce the flammability of the system.

The chemical processes involved in the production of phenol has several impacts on the environment. This effects on the environment are due to the different kinds of waste generated during the whole process. These wastes are

1. Acetophenone
2. Acidified water

These wastes are generated at the various stages of the process and have different impacts on the environment. Acetophenone is a major by-product of the whole system.

Acidified water is released from the processes that occur in the separation chamber. This waste is generated when the PH of water is lowered and due deposited through precipitation. The water disrupts the ecosystem and significant nutrient flow leading to the death of freshwater fish and plant that depend on PH conditions.

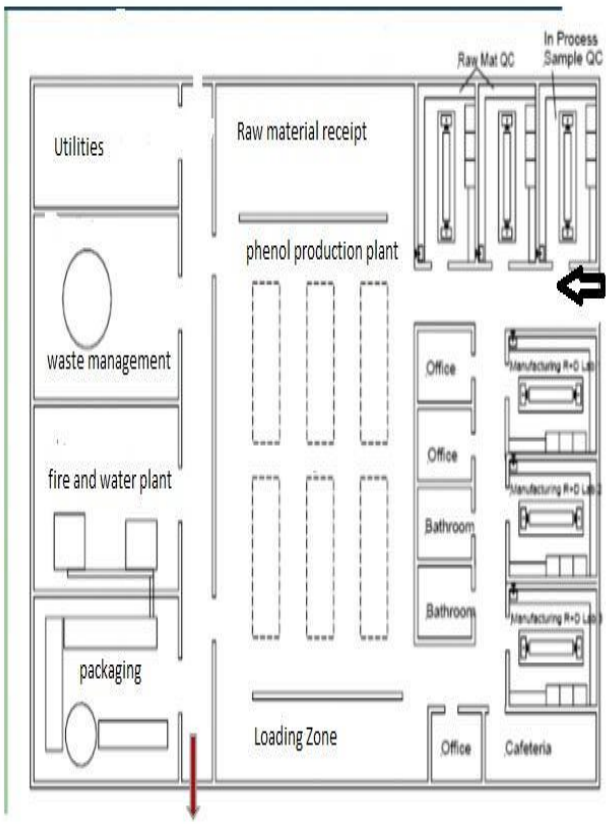
Properties of the acidified water include:

Physical properties	data
Chemical formula	H_2O
Physical state at room temperature	Liquid
Odor	-
Appearance	Colorless liquid
Boiling point	100°C
Melting point	0°C
Relative density	$1g/cm^3$
Molar mass	18.00 g/mol
solubility	Infinite
Viscosity	8.90 x 10-4 Pa.s
pH	3.0

From these environmental conditions, it is evident that the plant requires much water for the recycling process hence would be advisable that is located near a water source. This location is also supported by the fact that transport to international market will be made easy by waterways.

effluent is used to ensure fuel-rich operation and enable flaring.

The ground layout of the factory



The layout is designed that way so as to allow for the entrance of material

and leaving off the product in a convenient way. The factory is situated at the center of the layout to make it accessible from all the parts of the campus.

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