MANUFACTURING OF HYDROGEN USING ETHANOL STEAM REFORMING

A Project Report

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DECLARATION BY THE SCHOLAR

I hereby declare that this submission is my own and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any Degree or Diploma of the University or other Institute of Higher learning, except where due acknowledgement has been made in the text.

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CERTIFICATE

This is to certify that the thesis titled **MANUFACTURING OF HYDROGEN USING ETHANOL STEAM REFORMING** submitted by AMAN GARG (R900213008), RAHUL RAJ (R900213033), ROHIT MAHESHWARI (R900213036), to the University of Petroleum & Energy Studies, for the award of the degree of **BACHELOR OF TECHNOLOGY** in Chemical Engineering with Specialization in "REFINING AND PETROCHEMICALS" is a bonafide record of project work carried out by them under my supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

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ACKNOWLEDGEMENT

ABSTRACT

Hydrogen is being contemplated as the future fuel in view of the abundant availability of hydrogen bearing substances in nature, its high energy content (120.7 kJ/g), and its combustion without creating any environmental pollution. Pollution free sources for hydrogen generation and efficient conversion to useful energy are the two important factors controlling the development of hydrogen economy. Out of various liquid hydrogen sources, ethanol is a sustainable candidate because of its renewable nature, increasing availability, biodegradable nature, low toxicity, and ease of transport. It can be easily converted to a hydrogen rich mixture through catalytic steam reforming process. Further, ethanol steam reforming (ESR) is thermodynamically feasible and does not cause catalyst poisoning due to complete absence of S-impurities. However, the carbonaceous deposition during ESR is still an issue to make it sustainable for hydrogen generation. This review contains all parallel possible reactions besides the desired reactions, which can promote carbonaceous deposition over catalyst surface with respect to temperature. The role of operating conditions such as water and ethanol feed ratio and temperature with carbon generation were interrelated. The characterization of different carbon forms synthesized during ESR and the possible role of active catalyst into carbon synthesis mechanism was also considered. The contribution of precursor used for catalyst preparation, the role of active metals, the interaction between active metals for bimetallic catalyst, different kind of support prominently studied for ESR and their structural behaviors were also correlated. This review makes an attempt to critically summarize whole ESR process along with sizing and economy of the equipments.

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INTRODUCTION

Hydrogen is one of the most important raw materials in the chemical and petrochemical industries. Furthermore, it could also be considered as an attractive energy carrier with a reduced environmental impact. Then, it can offer an answer to the threat of global climate change and avoid undesirable issues associated with the use of fossil fuels. Hydrogen does not exist in nature in a form that can be collected and consumed but it can be currently produced by a number of processes such as natural gas or biogas reforming, gasification of coal and biomass, water electrolysis, photo-electrolysis and biological processes. Traditionally, large-scale production of hydrogen is mainly based on the methane reforming process. However, this pathway has a non-renewable nature as methane is mainly obtained from natural gas. Furthermore, together with hydrogen, other carbon derived products such as carbon monoxide and carbon dioxide are formed as side products. In this sense, there is a growing interest in the search for effective alternatives to produce hydrogen from renewable sources. In this regard, ethanol is very attractive because of its relatively high hydrogen content, broad availability, non-toxicity, secure storage and handling. In addition, it can be obtained from the fermentation of biomass. The catalytic steam reforming of ethanol is an endothermic process that requires external heat input:

$$C_2H_5OH + 3H_2O \longrightarrow 2CO_2 + 6H_2 \ (\Delta H = 173.1 \ kJ/mol) \qquad (1)$$

which could be supplied from external sources in order to maintain the system at a steady reaction temperature. Heat can also be supplied externally by the combustion of part of the feed, by burning combustible off gases or by a combination of both processes.

Additionally, the ethanol-steam mixture is catalytically converted to carbon monoxide according to the following reaction:

$$C_2H_5OH + H_2O \longrightarrow 2CO + 4H_2 \quad (\Delta H = 298.5 \ kJ/mol) \qquad (2)$$
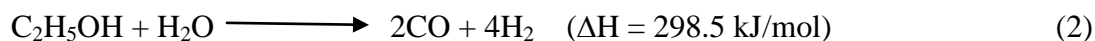
Hydrogen production via catalytic reforming of ethanol involves two more additional steps aimed at reducing the concentration of CO below the stringent levels required by hydrogen fuel cells operating downstream: the water gas shift reaction (WGS) and CO preferential oxidation

reaction (COPROX). WGS is an important step in which CO is generally oxidized to CO_2 in excess steam:

$$CO + H_2O \longrightarrow CO_2 + H_2 \ (\Delta H = -41 \ kJ/mol) \tag{3}$$
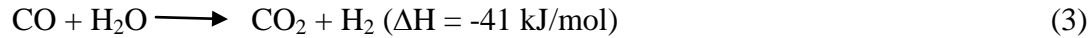
In the COPROX process, the following reactions occur in the gas phase:

$$CO + 1/2O_2 \longrightarrow CO_2 \ (\Delta H = -238 \ kJ/mol) \tag{4}$$

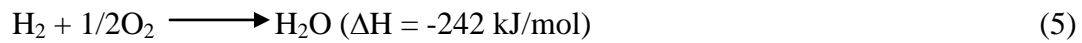$$H_2 + 1/2O_2 \longrightarrow H_2O \ (\Delta H = -242 \ kJ/mol) \tag{5}$$
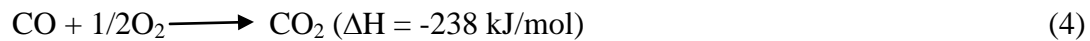
The final step is the purification of the hydrogen from the gas stream exiting the COPROX process, which can be accomplished using several techniques. The most common methods are: pressure-swing-adsorption (PSA) to separate CO_2 followed by the condensation of the remaining H_2O, PSA to separate H_2, and membrane separation of H_2 .Consequently, a production of high purity hydrogen by catalytic ethanol reforming is a complicated process including several reaction and separation steps.

x

LITERATURE SURVEY

Renewable energy resources have shown a peculiar attention at present global scenario owing to abnormal growth of population and development which leads to progressive depletion of conventional fossil fuels (coal, petroleum, natural gas). Among renewable energy resources, hydrogen (H_2) is considered as an important energy carrier for the future as it is abundantly available and contains the maximum energy per unit of weight (120.7kJ/g) of presently known fuels. Production of renewable hydrogen energy comprises thermo-chemical, electrochemical, photo-biological and photo-electrochemical methods. Among thermo-chemical technologies, steam reforming is most widely used to generate hydrogen not only with nonrenewable fossil fuels (Coal, natural gas, and petroleum) but also with renewable raw materials such as ethanol. In India large amount of molasses as by product from sugar industry can be reformed to renewable hydrogen. Molasses besides the renewable source of ethanol, it is advantageous as carbon lean fuel and non-hazardous over other conventional fossil fuels. Ethanol steam reforming (ESR) is an endothermic reaction and thus it requires heat energy to generate hydrogen. The major challenge is to minimize the heat energy. Catalysts play a significant role in minimizing the heat energy.

Three primary techniques can be applied to produce hydrogen from hydrocarbons: steam reforming (SR), partial oxidation (POX), and auto thermal reforming (ATR). Steam reforming is the most studied and used in industry since it has the highest hydrogen yield, and a H_2/CO ratio of about 3/1 would be produced.

The study of ESR over supported metal catalysts in the temperature range (873 - 1073K) by Liguras et. al (2003) suggested that at higher temperature conversion of ethanol as well as selectivity of CO, CO_2 and H_2 get increased (Liguras et al, 2003). At higher temperature reverse water gas shift reaction is only responsible reaction to lower down the H_2 yield (Lima et al, 2009). The theoretical calculation by Rabenstein et. al reveals relation between temperature and water to ethanol feed ratio. The molar feed ratio of ethanol and water higher than 4 at reaction temperature range (823-923K) able to produce more than 4 moles of H_2 (Rabenstein and Hacker,

2008). Selectivity of H_2 is increased considerably with increase in S/E molar ratio (Comas et al, 2004).

ESR was reported over noble metals (Pt,Pd,Rh,Ru), non noble metals (Ir,Cu,Co,Ni), metal oxides, mixed metal oxides, catalysts. Among non-noble metal catalyst Cu, Ni, Ir and Co were reported as most active metals (Duan and Senkan 2005). The nature of metal and support contributes the selection of path for hydrogen generation. Highly acidic nature of support facilitate dehydration (Fajardo and Probst, 2006) of ethanol whereas basic nature (La_2O_3, MgO, SiO_2) (Dominguez et al. 2010) or addition of promoters (alkali and alkaline earth metals) which reduce acidity (Hou et al, 2003), hinders dehydration and deactivation of catalysts by carbonaceous deposition. Among noble metal catalysts study of Liguras et. al (2003) shows the selectivity of H_2 over γ-Al_2O_3 support in the order as Rh $\gg$ Pt > Ru $\approx$ Pd. High activity and selectivity of Rh for ESR was also supported by work of Aupretre et. al(2002). Ru is inactive over γ-Al_2O_3 with lower than 5% loading but it shows 100% ethanol conversion with high selectivity over CeO_2/YSZ support on 2% loading (Ramos et al, 2012). The study reported by Frusteriet al (2004) over MgO support for Rh (3%) and Pd (3%) shows inferior activity as compared to Ni (21%) over similar support. Rh leads to methane formation during ESR and has relatively low efficiency as compared to Ni and Co for the SR of methane. The higher capability of nickel to break C-C and O-H bond and hydrogenation, leading to molecular hydrogen formation makes it a best option for ESR. Furthermore, addition of alkali and alkaline earth metals effects the interaction between metal and adsorbed species (Elias et al, 2013). Cobalt also shows higher activity for ESR but sintering at high temperature is major issues. Metallic cobalt sites are dynamic for ethanol decarboxylation and dehydrogenation reactions promoted by Co^{2+} leads to formation of acetaldehyde species (Hyman and Vohs 2011). Machocki et al. (2010) has reported the best ethanol conversion (100%) and H_2 (92.6%) selectivity over nanosized CeO_2 support at lower temperature.

METHODOLOGY

The simulation of the catalytic steam reforming and electrochemical reforming of ethanol–water mixtures processes was performed under stationary conditions using the flow sheeting simulator Aspen HYSYS (AspenTech V.7.1). Peng–Robinson equation was used to calculate the thermodynamic properties of each flow stream. This equation of state is widely used in reforming processes of ethanol and thus, it was used in this work for comparison purposes. The component list was restricted to C_2H_5OH, H_2O, H_2, CO, C_2H_4O, CO_2, CH_4, O_2, N_2 and C_2H_4 for the catalytic steam reforming and C_2H_5OH, H_2O, H_2 and C_2H_4O for the electrochemical reforming as experimentally confirmed. The reaction conditions for the catalytic steam reforming of ethanol were taken from literature data for a Pt/Al_2O_3 catalyst (1 wt.% metal loading). In the case of the electrochemical reforming of ethanol, catalysts based on Pt–Ru (40 wt.% Pt-20 wt.% Ru) and Pt (20 wt. % Pt), both supported on carbon, were used. The metal loading was of 1.5 mg cm^2 and 0.5 mg cm^2 for the Pt–Ru and Pt catalysts, respectively. As reported in literature, these metals have been typically used as the anode (Pt–Ru) and cathode (Pt) electrodes in electrochemical reforming reactors. The operating conditions and the polarization curves for the process simulation were also taken from literature.

The following assumptions were considered:

- Air water and ethanol were injected into the process at room conditions (T = 25 °C and P = 1 atm).
- The composition of atmospheric air was fixed at 21% O_2 and 79% N_2.
- 10% of excess air was used in the combustion furnace to heat the reforming reactor unit.
- 10% of excess air was used in the COPROX reactor unit for CO oxidation.
- The adiabatic efficiency of pumps and compressor was considered to be 80%.
- An average pressure drop of 9.807 kPa was considered for the heat exchangers, heaters and splitter.

- The reforming reactor and PEM reactor units were simulated as a conversion reactor using reported data.
- WGS and COPROX reactor were simulated as equilibrium reactors.

OBJECTIVE

1. Design of plant capacity based on hydrogen production
2. Material Balance
3. Energy Balance
4. Sizing of Equipments
5. Plant Economy

August-September
- Literature Survey

September-October
- Design of plant capacity based on hydrogen production

November-Decmber
- Material Balance
- Energy Balance

January-March
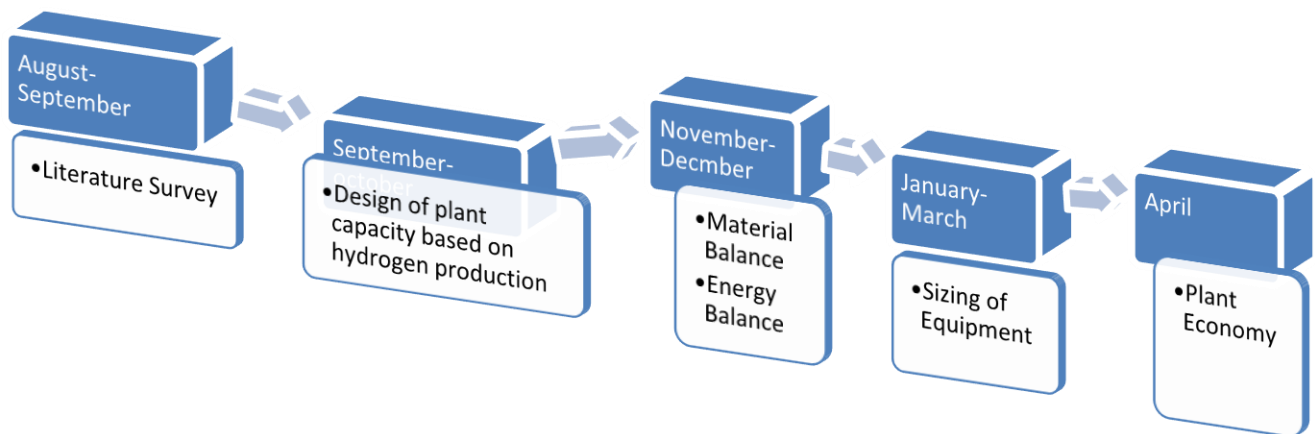- Sizing of Equipment

April
- Plant Economy

FIGURE 1

DESCRIPTION OF THE TOTAL WORK ALONGWITH TIME FRAME FOR ACTIVITY
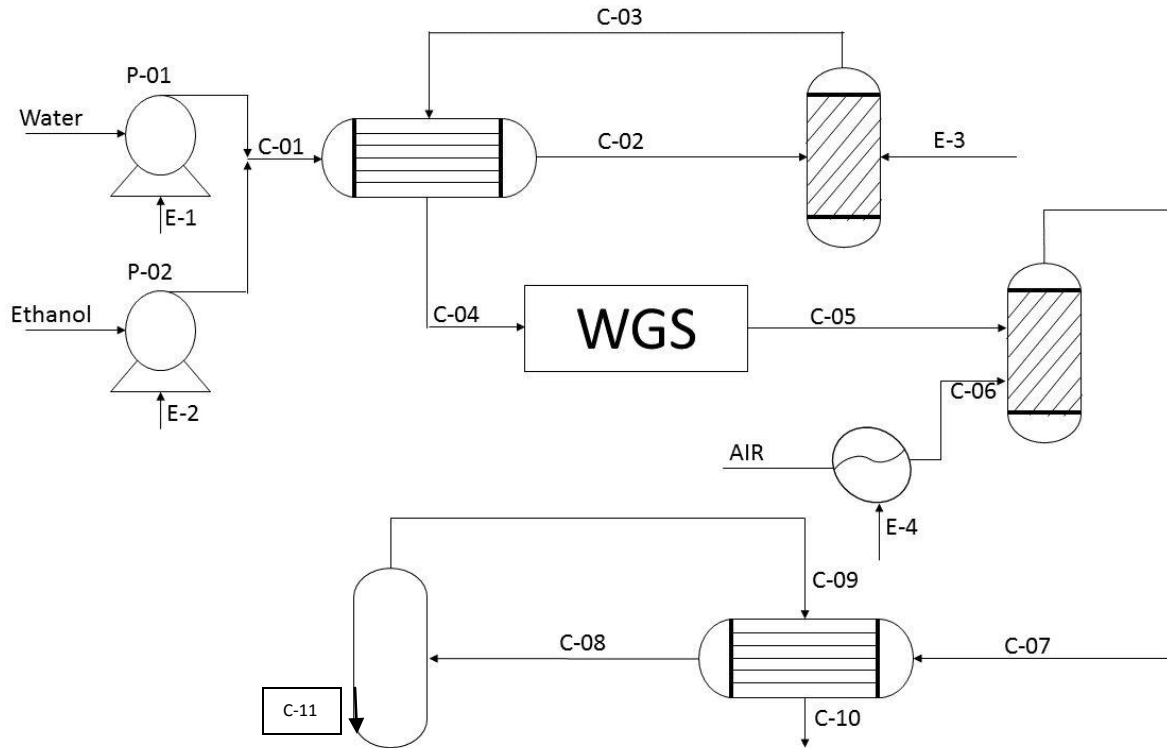
MATERIAL AND ENERGY BALANCE

FIGURE 2

 PROCESS FLOW DIAGRAM

Table 1

Description of the material and process energy for the catalytic steam reforming of ethanol–
water mixtures.

Material Streams/ Process Streams	Description
Water	Water input stream (room conditions)
Ethanol	Ethanol input stream (room conditions)
C-01	Water/ethanol mixture input at heat exchanger
C-02	Feed stream to the reforming reactor
C-03	Output stream from the reforming reactor
C-04	Feed stream to the water gas shift reactor
C-05	Feed stream to the CO preferential oxidation reactor (COPROX)
C-06	Air input to the COPROX
C-07	Output stream from the COPROX to heat exchanger
C-08	Input stream to the hydrogen purifier
C-09	Hydrogen stream input at heat exchanger
C-10	Pure hydrogen outlet
C-11	Output Stream from membrane process
E-01	Pump (P-01) electrical stream
E-02	Pump (P-02) electrical stream
E-03	Reforming reactor energy stream

Table 2

Molar balances of the catalytic steam reforming process.

Stream	Temp(°C)	P(atm)	H_2O	C_2H_5OH	H_2	CO_2	CH_4	CO	C_2H_4O	C_2H_4	Air
Water	25	1	736.6	-	-	-	-	-	-	-	-
Ethanol	25	1	-	122.7	-	-	-	-	-	-	-
C-01	25	2.5	736.6	122.7	-	-	-	-	-	-	-
C-02	290	2.2	736.6	122.7	-	-	-	-	-	-	-
C-03	800	1.8	705.69	49.1	144.29	20.61	22.08	41.22	22.086	9.57	-
C-04	400	1.7	705.69	49.1	144.29	20.61	22.08	41.22	22.086	9.57	-
C-05	170	1.5	664.89	49.1	185.09	61.41	22.08	0.4122	22.086	9.57	-
C-06	170	1.5	-	-	-	-	-	-	-	-	731.06
C-07	170	1.5	665.3	49.1	184.67	61.82	22.08	-	22.086	9.57	731.06
C-08	300	1.2	665.3	49.1	184.67	61.82	22.08	-	22.086	9.57	731.06
C-09	300	1.1	-	-	184.67	-	-	-	-	-	-
C-10	163	1	-	-	184.67	-	-	-	-	-	-
C-11	300	1.2	665.3	49.1	-	61.82	22.08	-	22.086	9.57	731.06

Table 3

To calculate specific heat capacities of different streams:

S. No.	COMPONENT	A	B (10^3)	C	D (10^-5)	(C^{ig}_p/R) 298 K
1	Ethanol	3.518	20.01	-6.002	0	8.948
2	Water	3.470	1.45	0	0.121	4.038
3	H_2	3.249	0.422	0	0.083	3.468
4	CO_2	5.457	1.045		-1.157	4.467
5	CH_4	1.702	9.081	-2.164	0	4.217
6	CO	3.376	0.557	0	-0.031	3.507
7	C_2H_4O	1.693	17.978	-6.158	0	6.506
8	C_2H_4	1.424	14.394	-4.392	0	5.325
9	Air	3.355	0.575	0	-0.016	3.509

Table 4

Specific heat capacities of streams at different temperatures:

COMPONENT	C_p(J/mol k) (800°C)	C_p(J/mol k) (400 °C)	C_p(J/mol k) (290° C)
ETHANOL	141.457	115.17	103.016
WATER	41.987	37.193	36.002
H_2	31.166	29.656	29.222
CO_2	52.827	46.673	44.763
CO	35.29	31.973	31.116
C_2H_4O	94.391	76.67	82.388
AIR	33.293	30.984	30.364
CH_4	72.702	56.563	50.172

Theoretical Calculations for table 1

TABLE 5

Base-case experimental parameters for catalytic steam reforming

UNITS	Reaction	Conversion (%)	Selectivity (%)
Steam Reforming Reactor (SMR)	$C_2H_5OH + 3H_2O \longrightarrow 2CO_2 + 6H_2$	8.4	14
	$C_2H_5OH + H_2O \longrightarrow 2CO + 4H_2$	16.8	28
	$C_2H_5OH + 2H_2 \longrightarrow 2CH_4 + H_2O$	9	15
	$C_2H_5OH \longrightarrow C_2H_4 + H_2O$	7.8	13
	$C_2H_5OH \longrightarrow C_2H_4O + H_2$	18	30

BASIS: 1 hour

For reaction 1 in steam reformer

C_2H_5OH reacting = (122.7*0.6*0.14)

$\qquad$ =10.3068 kmol

H_2 produced = (10.3068*6)

$\qquad$ =61.84 kmol

CO_2 produced = (10.3068*2)

$\qquad$ =20.61 kmol

For reaction 2 in steam reformer

C_2H_5OH reacting = (122.7*0.6*.28)

$\qquad$ = 20.6136 kmol

H_2 produced = (20.6136*4)

$\qquad$ = 82.45 kmol

CO produced = (20.6136*2)

$= 41.22$ kmol

For reaction 3 in steam reformer

C_2H_5OH used $= (122.7*.6*.15)$

$\qquad = 11.043$ kmol

H_2 used $= (2*11.043)$

$\qquad = 22.086$ kmol

CH_4 produced $= 22.086$ kmol

H_2O produced $= 11.043$ kmol

For reaction 4 in steam reformer

C_2H_5OH used $= (122.77*.6*.13)$

$\qquad = 9.5706$ kmol

C_2H_4 produced $= 9.5706$ kmol

H_2O produced $= 9.5706$ kmol

For reaction 5 in the reformer

C_2H_5OH used $= (122.7*.6*.3)$

$\qquad = 22.086$ kmol

H_2 produced $= 22.086$ kmol

C_2H_4O produces $= 22.086$ kmol

After Water Gas Shift Reactor (stream C-05)

For conversion of 99 %

CO reacting = (41.22*0.99)

$\qquad$ = 40.80 kmol

CO_2 produced = 40.80 kmol

H_2 produced = 40.80 kmol

COPROX Reactor

CO reacting = 0.4122 kmol

CO_2 produced = 0.4122 kmol

SIZING OF EQUIPMENTS

Heat exchanger

C_p(C-01) = 80.55 J/mol-k

C_p(C-03) = 30.269+6.952+3.753+1.195+2.161+0.685+2.877+1.152

   = 49.044 J/mol-k

C_p(C-04) = 42.682 J/mol-k

$C_{p\ avg}$(C-03 & C-04) = (49.044+42.682)/2

      = 45.863 J/mol-k

Head load = (999000*42.682*(800-400))/3600

   =4737.7 kW

ΔT_{ln} = ((800-290)-(400-25))/ ln((800-290)/(400-25))

   = 439.04 °C

R = (800-290)/(290-25)

  = 1.92

S = (290-25)/(800-25)

  = 0.34

F_t = 0.86 (From Graph)

ΔT_m = 439.04* 0.86 = 377.57 °C

From given requirements,

U = 250 W/m^2 °C

Area Required = 4737700/(250*377.57)

$$= \mathbf{50.19 \ m^2}$$

Steam Reformer

Applying mass balance equation,

$$M_{in} - M_{out} + V*(-r_A) = \text{Accumulation}$$

Accumulation = 0   (Steady state)

M_{in} = 859.3 Kmol/hr

M_{out} = 999 Kmol/hr

$$C_{Ao} = F_{Ao} / v_o$$

For $\mathbf{v_o}$:

M = 21.99 gm/mol

ρ = 969.79 kg/m^3

$$v_o = (859.3*21.99) / 969.79$$

$$= 19.488 \ m^3/hr$$

For ethanol:

F_{Ao} = 122.7Kmol/hr

F_A= 49.1 Kmol/hr

C_{Ao} = 122.7/19.488

= 6.29 mol/l

$C_{Af} = 49.1/19.488$

$\quad = 2.51 \text{ mol/l}$

$C_{Af} = C_{Ao}(1-X_A)$

$2.51 = 6.29(1-X_A)$

$X_A = 0.6009$

By mass balance equation,

$999-859.3 = V*K*C_{Af}$

$V*K = 55.657$

Taking rate constant of the reaction (K) = 0.3 /hr

V = **185.52 litres**

Therefore, Volume of the reformer = 185.52 litres

PLANT ECONOMY

Shell and Tube Heat exchanger

Governing equations for cost estimation

SI Units

$$C_B = EXP(8.202 + 0.01506*lnA + 0.06811*(lnA)^2)$$

where:

C_B = Base Cost of the HE, USD

A = Heat Transfer Area in m^2

Lower Limit: 14 m^2; Upper Limit: 1100 m^2

Exchanger-type cost factor, F_D

Fixed Head:

$$F_D = EXP(-0.9003 + 0.0906*lnA)$$

Design-pressure cost factor, F_P

$$F_P = 0.8955 + 0.04981*lnA$$

Material-of-Construction Cost Factor, F_M

SS316:

$F_M = 1.4144 + 0.23296*lnA$

Heat-Exchanger Cost , C_E

$C_E = C_B*F_B*F_D*F_M$

where:

C_E = Heat Exchanger Cost, USD

Using above equations,

(For A= 50.19 m^2)

C_B = exp (8.202+ 0.05897+1.04437)

$\qquad$ = 10996.59 USD

F_D = exp (-0.9003+0.3547)

$\quad$ = 0.5795

F_P = 0.8955+0.1950

$\quad$ = 1.0905

F_M = 1.4144 + 0.1922

$\quad$ = 2.3266

$C_E = 10996.59 * 0.5795 * 1.0905 * 2.3266$

$\quad = 16,168.10$ USD

TABLE 6

COST ESTIMATES FOR EQUIPMENTS

EQUIPMENT	TYPE	QUANTITY	MATERIAL	COST (USD)
Reformer	Fixed Bed	1	Incoloy	28,746
Shift Reactor	Fixed Bed	1	316 SS	20,594
Pressure Swing Adsorber	Fixed Bed	1	316 SS	4.830
Heat Exchanger	Shell and Tube	2	316 SS	32,300
COPROX unit	Fixed Bed	1	316 SS	5,270
Natural Gas Compressor	Centrifugal	1	Carbon Steel	3,354
Water Pump	Pos. Displacement	1	Carbon Steel	3,210

Projected Cost = $98,304

RESULTS AND DISCUSSION

In order to suggest an optimized catalytic system for hydrogen production via ethanol steam reforming, many factors need to be taken into account, such as the type of active metal catalyst, the type of catalyst support, and the presence of promoters as well as the reaction condition, that is water-to-ethanol molar ratio, temperature and space velocity.

Sizing of the major equipments in the manufacturing unit as shown in the process flow diagram has been done. Accordingly, the projected cost for the installation of the equipments as per the material of construction, their area and volume has been calculated.

The cost of installation changes as per the material of construction, the capacity, catalysts and various other factors. The cost of equipments are found on basis used in NREL, USA in a small scale plant.

The cost was found after calculating the plant capacity by doing material and energy balance of each unit in the process flow diagram. The temperature of streams is calculated and the heat recovery by the heat exchangers is done and then the capacity of the plant for producing hydrogen is done.

CONCLUSION

The catalytic steam reforming of ethanol is a promising route for the sustainable production of hydrogen for using fuel cells. For this process, the catalyst must be stable, active, selective, and maximize hydrogen production by minimizing the generation of by-products, such as CO and CH_4. Out of various liquid hydrogen sources, ethanol is a sustainable candidate because of its renewable nature, increasing availability, biodegradable nature, low toxicity, and ease of transport. It can be easily converted to a hydrogen rich mixture through catalytic steam reforming process. Further, ethanol steam reforming (ESR) is thermodynamically feasible and does not cause catalyst poisoning due to complete absence of S-impurities.

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