

DESIGN OF MULTI-TUBULAR PACKED BED REACTOR FOR ETHANOL STEAM REFORMING TO PRODUCE HYDROGEN

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ABSTRACT

Steam reforming is a method for producing hydrogen, carbon monoxide, or other useful products from hydrocarbon fuels such as natural gas. This is accomplished in a preparing gadget called a reformer which responds steam at high temperature with the petroleum derivative. The steam methane reformer is broadly utilized in industry to make hydrogen. The present study has been conducted to explore the options of how hydrogen can be produced most effectively. There is additionally enthusiasm for the improvement of a lot littler units dependent on comparative innovation to deliver hydrogen as a feedstock for power modules. Little scale steam improving units to supply power devices are as of now the subject of innovative work, regularly including the changing of methanol, however different fills are likewise being viewed as, for example, propane, gas, auto-gas, diesel fuel, and ethanol. ASPEN PLUS(V8.6) is the software that has been used for this simulation process. ASPEN PLUS is a product bundle intended to enable a client to construct a procedure model and afterward reenact the model without repetitive computations.

Key Words : Steam reforming, Hydrogen, Petroleum, Feedstock, Aspen plus, Simulation, Reformer

INTRODUCTION

Hydrogen creation from biomass has pulled in incredible intrigue due to the potential application in power devices. The utilization of bio-powers for the creation of hydrogen additionally gives significant natural benefits, since the delivered CO₂ is expended for biomass development and in this manner offering a carbon dioxide unbiased vitality supply.¹ Hydrogen can be created by steam improving of the biomass inferred oxygenates. Bioethanol is promptly created by aging of starch and sugar or lowercost crop squanders and steam improving of bioethanol has been generally explored over bolstered progress and honorable impetuses. In the interim, significant measure of glycerol are delivered asaby-product during bio-diesel production by transesterification of vegetable oils, which are acces-

sible requiring little to no effort in huge supply from sustainable crude materials. The promising method to use this weakened glycerol watery arrangement is to deliver hydrogen by steam changing. In any case, the steam improving responses of these bio-oxygenates is regularly joined by the arrangement of different side-effects, which enormously influence the particular generation of hydrogen and lead to quick deactivation of the impetuses due to the disjoin coke statement.²⁻⁴

Steam changing of ethanol happens as per the stoichiometric response, $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$. The response may happen through development of CO as a middle of the road item, which is along these lines changed over into CO₂ by the water gas move response ($CO + H_2O \rightarrow CO_2 + H_2$). Ni impetuses indicated

great introductory action for ethanol steam improving, yet before long displayed higher methane arrangement as side-effect and quick deactivation due to the separate coke affidavit. Co impetuses gave very articulated execution in hydrogen creation from ethanol transforming and proposed as fitting frameworks, while the significant deactivation through sintering and surface cobalt oxidation restricted the application to the responses performed even at moderate temperatures.⁵⁻⁶

Multi-tubular packed bed reactor

Originally fixed bed reactors, later in the form of multi-tubular fixed bed reactors, were used for LTFT operations. At present, multi-tubular fixed bed reactors are commercially operated by Sasol in South Africa and by Shell in Malaysia using iron-and cobalt-based catalysts, respectively. These reactors typically operate between 180–250 °C at pressures ranging from 10–45 bar, although even higher pressures might be attractive to further increase the capacity of a single reactor. Under such conditions, the reactor operates in the three-phase gas–liquid–solid trickle bed mode. Heat gets removed through the tube walls to generate steam on the shell side of the reactor. The interaction between heat generation and heat removal through the walls gives rise to axial and radial temperature profiles. The effective control of temperatures and prevention of unstable conditions become more critical with increasing activity of the catalyst. When the options to increase heat transfer through gas and liquid recycle have been exhausted, further improvements can only be achieved by decreasing the tube diameters, which will escalate the reactor cost. Besides difficult heat management, other disadvantages of multi-tubular fixed bed reactors include the inability to replace catalyst during production, the relatively high pressure drop and the occurrence of significant intra-particle diffusion limitations.⁷

Catalyst selection

After an exhaustive study involving different catalysts like Ni/CeO₂, Ni/Al₂O₃, CO/CeO₂ and quite a few others, the catalyst selected for this simulation was the Nickel (II)-Aluminum (III)-Double Hydroxide- Lamellar catalyst.

Layered twofold hydroxides (LDH) are a class of ionic solids described by a layered structure with the conventional layer succession [AcB Z AcB]_n, where c speaks to layers of metal cations, An and B are layers of hydroxide(HO⁻) anions, and Z are layers of different anions and nonpartisan atoms, (for example, water). Parallel balances between the layers may result in longer rehashing periods.

This catalyst has been used because it gives us high conversion at relative low porosity and catalyst density and is also relatively cheap.

Ni(II)– Al(III)– LDH impetus forerunner, from this point forward named NiAl, was orchestrated by the urea strategy, maturing blended aluminum(III)– nickel(II)– urea arrangements at 363 K in screwcapped plastic containers, which were set in a thermostated water shower preheated at working temperature for 24 h. The molar proportion Ni(II)/Al(III) in the arrangement was 2.33, esteem normal of takovite. After this time, bottles were drenched in an ice-water shower to extinguish the response. Hastened strong was gathered by centrifugation, washed with virus water, and dried medium-term at 343 K. Prior to response, a NiAl test was submitted to a decrease treatment in a flow of unadulterated hydrogen at T = 923 K. This example was portrayed by synthetic examination, sorptometry, TGA and XRD estimations. The diminished NiAl test had a specific zone of 100 m²/g and the mean size of the Ni metallic crystallites was evaluated utilizing Scherrer's condition, being near 5 ± 1 nm. More subtleties of union and portrayal of NiAl test are given somewhere else.

Kinetic model

The kinetic model used for this process is the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model. Different models like the Elay-Riedal Model, LHHW model etc. can be used for simulating the reaction kinetics. Here we have used the LHHW model due to its functional simplicity and effectiveness.^{8,9}

METHODOLOGY

Simulation tool used :

Aspen PlusTM (from Aspen technology)

Equipments/ Materials used in simulation:

Packed Bed Reactor (Multi-tubular), Ethanol,

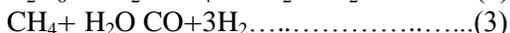
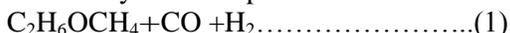
Steam, Suitable catalyst (Ni, Co or Ir over Cerium support is used in this case).

Procedure:

- Catalysts preparation and characterization (Ni-Al-LDH catalyst).
- Catalytic test.
- Design and Simulation on Aspen Plus using all the required data and inputs.
- Study of the variation of length and percentage conversion using the different catalyst.
- Simulation is performed and established the condition for the best and most efficient production of Hydrogen gas from Ethanol and water.
- The EOS model for the project simulation is based on the Peng-Robinson EOS.

RESULTS AND DISCUSSION

The kinetics of the ESR is based on a four reaction system comprises as follows:



Surface reaction will be considered as RDS in Equas 1-4 and

the corresponding kinetic expressions are:

$$r_1 = \frac{k_1^+ C_i K_E P_E}{1 + P_E K_E + P_W K_W + P_M K_M}$$

$$r_2 = \frac{k_2^+ C_i^2 K_E K_W P_E P_W}{(1 + P_E K_E + P_W K_W + P_M K_M)^2}$$

$$r_3 = \frac{k_3^+ C_i^2 K_M K_W (P_M P_W - \frac{P_{CO} P_{H_2}^3}{K_3})}{(1 + P_E K_E + P_W K_W + P_M K_M)^2}$$

$$r_4 = \frac{k_4^+ C_i^3 K_M K_W (K_W P_M P_W^2 - \frac{P_{CO_2} P_{H_2}^4}{K_4})}{(1 + P_E K_E + P_W K_W + P_M K_M)^3}$$

The kinetics is modeled on the LHHW (Langmuir-Hinshelwood-Hougen-Watson) model. The kinetic data has been calculated from different research papers and is given in **Table 1** :

Table 1 : LHHW model kinetic data

Reaction kinetics			KJ/mol	ln(ki0)	Ea/R				
k10	3.27E+14	Ea1	2.72E+02	33.42098129	3.27E+04				
k20	1.39E+13	Ea2	2.27E+02	30.26290996	2.73E+04				
k30	2.21E+06	Ea3	1.23E+02	14.60723159	1.48E+04				
k40	1.26E+12	Ea4	2.14E+02	27.86213284	2.57E+04				
Adsorption constants		ln(KE0)							
KE0	1.14E-04	-9.07931	HE	-9.17E+01	HE/R	1.10E+04			
KW0	6.98E-11	-23.3854	Hw	-1.98E+02	Hw/R	2.38E+04			
KM0	3.96E-05	-10.1367	Hm	-1.25E+02	Hm/R	1.50E+04			
Equilibrium constants									
ln(K30)	2.93E+01	H3/R	-2.62E+04	K30	5.3E+12	ln(1/K30)	-29.2987	K30	5.30E+12
ln(K40)	2.50E+01	H4/R	-2.16E+04	K40	7.20E+10	ln(1/K40)	-24.9999	K40	7.20E+10

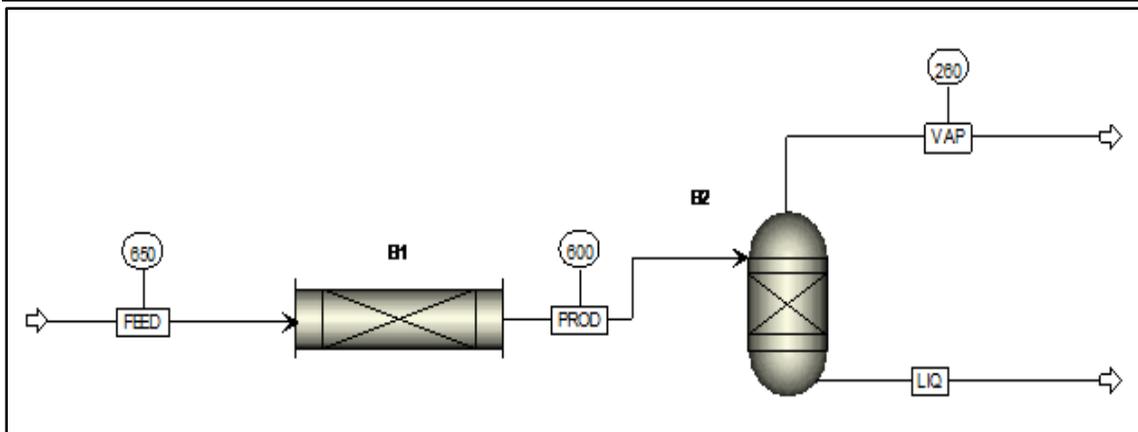


Fig. 1 : Reactors

Table 2 : Simulation results

Heat and Material Balance Table					
Stream ID		FEED	LIQ	PROD	VAP
From			B2	B1	B2
To		B1		B2	
Phase		VAPOR	MISSING	VAPOR	VAPOR
Substream: MIXED					
Mole Flow	kmol/hr				
ETHAN-01		.0700000	0.0	0.0	0.0
WATER		.2100000	0.0	.0950534	.0243702
CARBO-01		0.0	0.0	.0951405	.0244573
CARBO-02		0.0	0.0	.0449113	.1155946
METHA-01		0.0	0.0	0.0	0.0
HYDRO-01		0.0	0.0	.3250336	.3957168
Total Flow	kmol/hr	.2800000	0.0	.5601390	.5601390
Total Flow	kg/hr	7.008042	0.0	7.009108	7.009108
Total Flow	l/min	198.8323	0.0	376.6012	229.9529
Temperature	C	649.8500		599.8500	259.8500
Pressure	bar	1.800000	1.800000	1.800000	1.800000
Vapor Frac		1.000000		1.000000	1.000000
Liquid Frac		0.0		0.0	0.0
Solid Frac		0.0		0.0	0.0
Enthalpy	cal/mol	-49283.05		-17418.09	-21264.32
Enthalpy	cal/gm	-1969.060		-1391.982	-1699.357
Enthalpy	cal/sec	-3833.126		-2710.154	-3308.605
Entropy	cal/mol-K	-7.417465		11.11591	5.577486
Entropy	cal/gm-K	-.2963581		.8883377	.4457296
Density	mol/cc	2.34704E-5		2.47892E-5	4.05981E-5
Density	gm/cc	5.87433E-4		3.10192E-4	5.08010E-4
Average MW		25.02872		12.51316	12.51316
Liq Vol 60F	l/min	.1310432	0.0	.4437445	.4855746

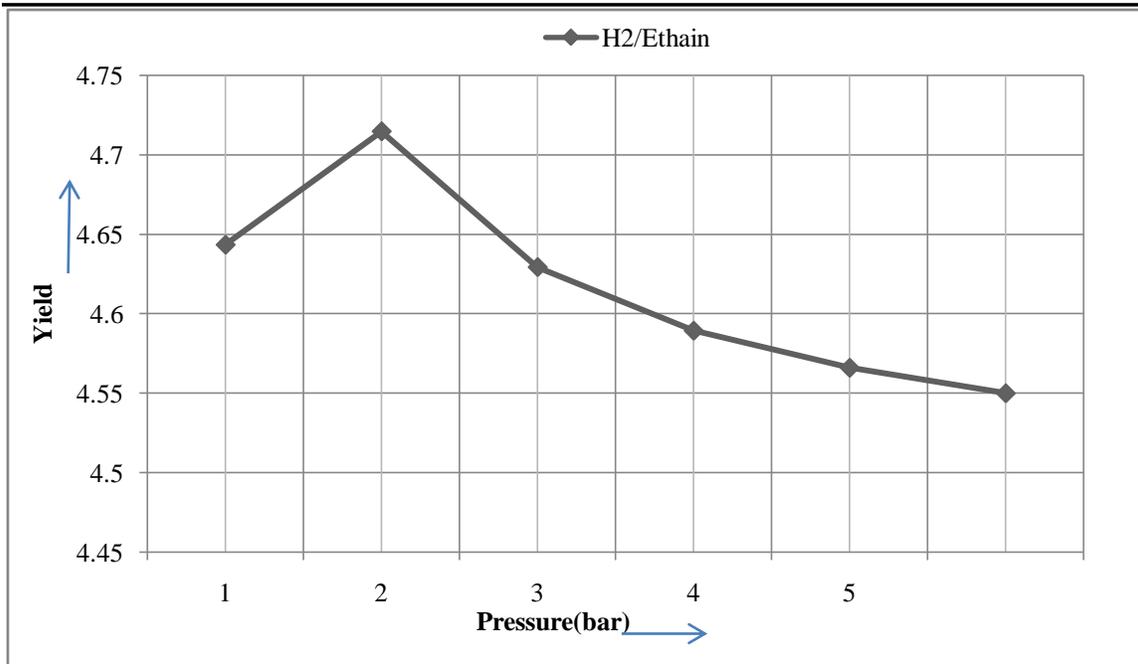


Fig. 2 : Yield vs. Pressure for H₂

Fig. 1 shows reactor used during the experiment. Eventually simulation results are given in Table 2.

Fig. 2 shows the graph between H₂/Ethanol input ratio (yield) v/s pressure for a pressure range of 1-5 bar. From this graph we conclude that the yield is maximized at a pressure of 2 bar if we

keep the temperature and Steam/Ethanol (S/E) ratio constant.

Fig. 3 shows the graph details for comparative study of yield variation at different temperature along the length of the reactor with a constant density and voidage-specified catalyst.

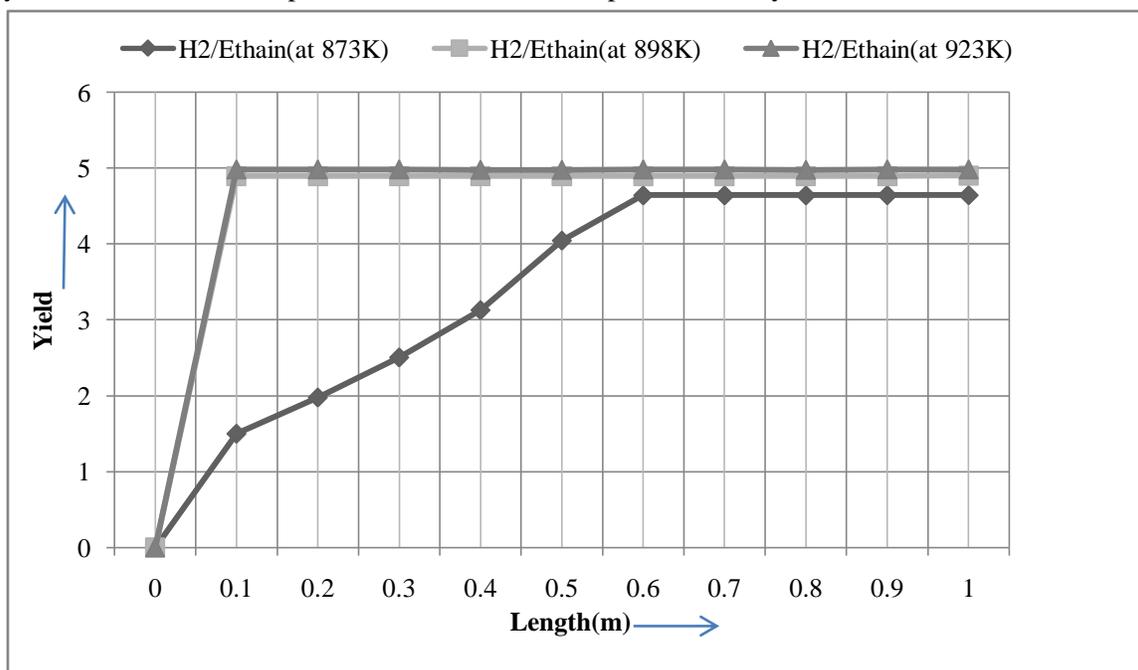


Fig. 3 : Yield vs. Length for H₂

The S/E ratio is taken constant at 3. We can conclude from this graph that there is a marked increase in the yield when the temperature is increased from 873 to 898K, change being measured along the length of the reactor as mentioned in Fig. 4.

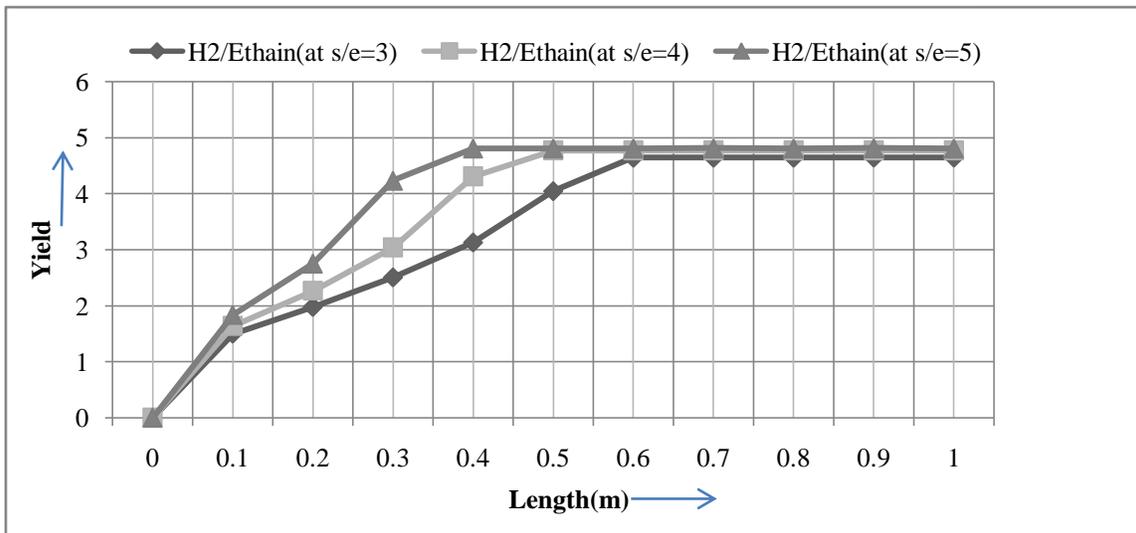


Fig. 4 : Yield vs. Length for H₂(at 873K)

Fig. 5 shows the graph for change of yield at different S/E ratio taken along the length of the reactor. The clear conclusion that can be drawn here is that the yield increases as the S/E ratio is increased from 3 to 5. Temperature here is taken 873K.

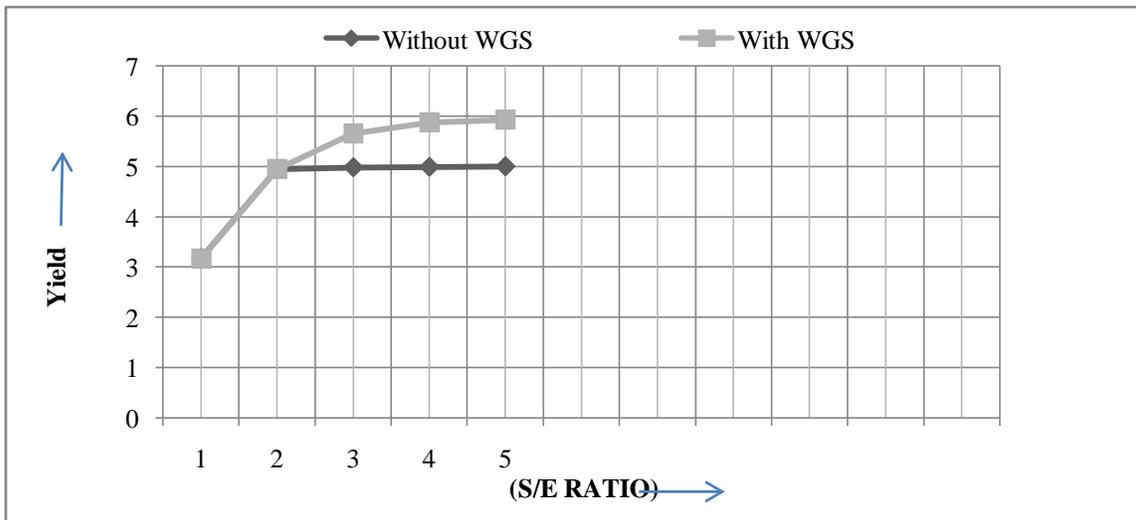


Fig. 5 : S/E ratio variation

GSR (Water Gas Shift Reaction) increases the production of hydrogen while eliminating carbon monoxide, a toxic pollutant from the system. This graph clearly shows an increase in the yield of H₂ w.r.t Ethanol while using a reactor to simulate the water gas shift reaction, as opposed to using no reactor. (Graph shows yield increase with increasing S/E ratio). (S/E is taken as 3).

CONCLUSION

A kinetic study of ethanol steam reforming using a Ni based catalyst was carried out. This catalyst, working in steady state, does not produce acetaldehyde or ethylene. Although the reaction rates involved are very fast, kinetic model was presented using the Langmuir–Hinshelwood approach and given

the experiment is performed at different water and ethanol concentrations; the RDS for each reaction involved is the surface reaction. A general model was valid for a wide range of water/ethanol feed ratio and of temperatures. This model considered a system of four series-parallel reactions involving all the products (CH₄, CO, CO₂ and H₂). The simulation is performed at various temperature and steam to ethanol ratios. We obtain a temperature of 898K at which the maximum conversion with length of 0.5m is achieved with steam to ethanol ratio of 4. We added a WGS reactor with product stream which reduces the CO and CO₂ in vapour stream and increases the hydrogen production. We did a comparative analysis of yield with and without having a WGS reactor by varying the S/E ratio. So we obtain a S/E ratio of 4 as giving us a better yield. So to get better yield in ethanol steam reforming system this model is performed at 898K temperature with having steam to ethanol ratio of 4. To reduce the cost of operation, system should be operated at low pressure.

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