Differentiate with respect to W and rearrange

$$\frac{dFA}{dW} = rA'$$

The Space time**,** tau, is obtained by dividing the reactor volume by the volumetric flow rate entering the reactor:

$$\tau = \frac{V}{v0}$$

Space time is the time necessary to process one volume of reactor fluid at the entrance conditions.

Calculation steps

1) Analyzing gas composition at the inlet of reactor at given temperature and pressure. It is done by Gas chromatography analysis.

Sr. No.	Component	Volume %
1	Methane	14.08
2	Ethane	4.03
3	Propane	0.089
4	n-butane	0.0061
5	i-butane	0.015
6	Ethylene	0.9
7	Hydrocarbon	5
8	Nitrogen	38.1
9	Hydrogen	32.89
10	Carbon monoxide	4.89

Table (1): Gas composition at the inlet of reactor

For ideal gas volume percentage is equal to mole percentage so next step is to find the compressibility factor z to determine state of gas at given temperature and pressure.

2) Find compressibility factor for gas component.

In our experimental cracking work consist of hydrocarbon gases mixture. Considering the non ideal behavior of the gas component we need to introduce compressibility factor which is denoted by Z.

It is denoted by

Z= P*V/n*R*T

Where P= pressure, in Kpa or mm Hg or mmWc

T = Temperature in Kelvin

V = Volumetric flow rate in m^3/hr

n = molar flow rate in mol/hr.

R =Universal gas constant   =8.314 J/mol. K

If Z=1 for prevailing condition than gas behaves ideally, otherwise it acts as a real gas. For i^{th} component its value is

$Z_i = Z_{0i} + \omega i * Z_{1i}$ ------eq. 1

Value of Z_0 and Z_1 is obtained from table 1[10] and table 2[10] for given reduce T and P.

3)   Molar flow rate of individual component can be found by the following equation.

$F_{i,0} = P0 * v_{i,0} / Z * R * T0$ ------eq. 2

4) Since compressibility factor for hydrocarbon gas is nearer to 1 we can say gas behavior is ideal one and total molar flow rate and mole fraction can be found by following equation.

5) $F_{t,0} = \sum F_{i,0}$ -------eq. 3

6) $Y_{i,0} = F_{i,0}/F_{t,0}$ -------eq. 4

Component	Tc	Pc	Pr	Tr	Vc	Zc	ω	Z_0	Z_1
Methane	190.56	4.599	0.0188	4.32	.098	.286	0.0115	1.000	1.000
Ethane	305.32	4.872	0.0177	2.69	.145	0.28	0.0995	0.999	0.0006
Propane	369.84	4.248	0.0204	2.22	0.2	0.27	0.1523	0.999	0.0018
Butane	425.12	3.796	0.0228	1.93	0.22	0.27	0.2002	0.999	0.002
Pentane	475	3.5	0.0247	1.73	0.29	0.27	0.25	0.999	0.002
Hexane	507.6	3.202	0.0270	1.63	0.37	0.26	0.3013	0.997	0.0038

Table (2): Calculation of compressibility factor Z
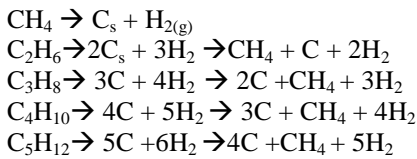
Variable of our study are as follow.

1) Temperature
2) Volumetric flow rate of gas at inlet. Decomposition reaction time for fixed temperature and volumetric flow rate.
3) Weight of catalyst.
4) Concentration in Mol/m3 of gas at inlet can be determined as follow.

   $C_{i,0} = F_{i,0}/ v_{,0}$ -----eq. 5

5) For given flow rate and temperature, pressure gas individual component detail is completely determined and presented in table 3.

| CALCULATION OF MOLAR/MASS FLOWRATE OF GAS					
AT INLET					
P0	700		mm Hg		
T0	823		K		
Component	volumetric flow rate ϑa0	Molar flow rate Fa0 mol/hr = P0*ϑa0/Z*R*T0	mol fraction	Concentration mol/m3	mass flow rate ,inlet gm/hr
CH4	0.141	1.920	0.141	1.920	30.727
C2H6	0.040	0.550	0.040	0.550	16.490
C3H8	0.001	0.012	0.001	0.012	0.534
n-C4H10	0.000	0.001	0.000	0.001	0.048
i-C4H10	0.000	0.002	0.000	0.002	0.119
C2H4	0.009	0.123	0.009	0.123	3.437
H.C.	0.050	0.682	0.050	0.682	58.650
N2	0.381	5.197	0.381	5.197	145.506
H2	0.329	4.486	0.329	4.486	8.972
CO	0.049	0.667	0.049	0.667	18.675
ϑ0	1.000	13.639	1		283.159

Table (3): Gas material balance data at the inlet of reactor

6) Reaction mechanism strongly suggests that operating pressure should be as low as possible, because the moles of product formed after the reaction is higher than reactant. Considering 60 % conversion of 1m3/hr

hydrocarbon into hydrogen and carbon at 823 K and 700 mm Hg pressure the hydrogen production and concentration at the outlet can be found as under:[11,12,13]

$CH_4 \rightarrow C_s + H_{2(g)}$

$C_2H_6 \rightarrow 2C_s + 3H_2 \rightarrow CH_4 + C + 2H_2$

$C_3H_8 \rightarrow 3C + 4H_2 \rightarrow 2C + CH_4 + 3H_2$

$C_4H_{10} \rightarrow 4C + 5H_2 \rightarrow 3C + CH_4 + 4H_2$

$C_5H_{12} \rightarrow 5C + 6H_2 \rightarrow 4C + CH_4 + 5H_2$

In general Hydrocarbon cracking or decomposition can be expressed in term of

$C_nH_{2n+2} \rightarrow nC + (n+1)H_2$
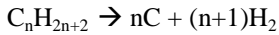
For known volumetric flow rate Material balance across the packed bed reactor for individual component is as under:-

Moles of i $|_{inlet}$ - Moles of i $|_{outlet}$ = Moles of ith component converted.

Component	H2 produced Mol/hr	C produced Mol/hr	H2 produced gm/hr	C produced gm/hr
CH4	2.3045	1.1523	4.6091	13.8272
C2H6	0.9894	0.6596	1.9788	7.9153
C3H8	0.0146	0.0146	0.0291	0.1748
n-C4H10	0.0025	0.0020	0.0050	0.0240
i-C4H10	0.0061	0.0049	0.0123	0.0589
C2H4	0.1473	0.1473	0.2946	1.7677
H.C.	2.8643	2.4551	5.7286	29.4614
N2	0.0000	0.0000	0.0000	0.0000
H2	0.0000	0.0000	0.0000	0.0000
CO	0.0000	0.0000	0.0000	0.0000
90	6.3288	4.4358	12.657	53.229

Table (4): Component converted inside the reactor

Moles of component, its concentration depend upon the amount converted in the catalyst bed.

Since there is increase in the mole of product than reactant we also have to determine two factor that is δi and εi for individual component.

For Reaction A $\rightarrow$ b/a B + c/a C

$\delta i = b/a + c/a -1$ ------eq. 6

$\varepsilon i = \delta i * y_{i,0}$ ------eq. 7

9) Concentration of reactant at the outlet of the reactor is determined by the following formula

$C_i = C_{i,0} * (1-X)/(1+\varepsilon i * X) * p/p_0$ ------eq. 8

Or

$C_j = C_{T0} * (F_j / F_T) * (P / P_0) * (T_0/ T)$

For given inlet volumetric flow rate of gas and conversion value of δi and εi is as shown in table 5.

Component	δi	εi
Methane	2	0.2815
Ethane	4	0.1612
Ethylene	3	0.027
Propane	4	0.00356
Butane	8	0.027
Hexane	12	0.6

Table (5): δ and ε value of gas component.

Component	volumetric flow rate $\vartheta a=Fa*Z*R*T/P$ mol/m3	Molar flow rate mol/hr $Fa=Fa0*(1-X)$	mol fraction	Concentration mol/m3	$Ca=Ca,0*(1-X)/(1+\varepsilon X)*p/p0$ mol/m3	mass flow rate,outlet gm/hr	Avg molecular weight gm/mol
CH4	0.0616	0.7682	0.0427	0.5324	0.5324	12.2908	0.6830
C2H6	0.0176	0.2199	0.0122	0.1524	0.1524	6.5961	0.3666
C3H8	0.0004	0.0049	0.0003	0.0034	0.0034	0.2136	0.0119
n-C4H10	0.0000	0.0003	0.0000	0.0002	0.0002	0.0193	0.0011
i-C4H10	0.0001	0.0008	0.0000	0.0006	0.0006	0.0475	0.0026
C2H4	0.0039	0.0491	0.0027	0.0340	0.0340	1.3749	0.0764
H.C.	0.0219	0.2728	0.0152	0.1890	0.1890	23.46000	1.3037
N2	0.4167	5.1967	0.2888	3.6014	3.6014	145.50665	8.0862
H2	0.8672	10.8148	0.6010	7.4948	7.4948	21.62696	1.2020
CO	0.0535	0.6670	0.0371	0.4622	0.4622	18.67752	1.0378
ϑ(m3/hr)	1.4430	17.9944	1.0000			229.813 5	12.7714

Table (6): Component stream at the outlet of the reactor

Once the concentration of the gas at the outlet is known for given condition we can either find the weight of catalyst needed for given conversion provided that rate constant value of each component is known or we can find the rate constant for given weight of catalyst and conversion.

By using characteristics equation for packed bed reactor [9]

$\frac{dXa}{dW} = \sum_{i=1}^{i=n} \frac{ra'}{Fa,0}$ -----eq. 9

Since decomposition of hydrocarbon lighter than gasoline obey first order reaction rate law, we can estimate the rate constant and activation energy as well as pre exponential factor or the weight of catalyst for given conversion.

11) Ergun equation is used to calculate Pressure drop calculation in porous bed. Ergun equation can be used for laminar as well as turbulent flow in the packed bed.[9]

$\frac{dP}{dZ} = \frac{-G}{\rho Dpgc} * \frac{(1-\phi)}{\phi3} * [\frac{150(1-\phi)\mu}{Dp} + 1.75G]$ ----eq. 10

Where

P= pressure, lb/ft^2

ϕ = Porosity= volume of void/total bed volume

1-ϕ = volume of solid/ total bed volume.

gc = 32.174 $lbm.ft/s^2.lbf$

Dp = diameter of particle in the bed, m

μ = viscosity of gas passing through the bed, lbm/ft.h(kg/m.s)

z= length down the packed bed of pipe, ft.

u= superficial velocity= volumetric flow / cross sectional area of pipe, ft/hr.

ρ=gas velocity, kg/m^3.

G= ρ*u = superficial mass velocity, kg/m^2.sec

Pressure drop in the across the bed is measured by u tube manometer filled with water. Temperature of the gas inlet, outlet and bed is measured by thermocouple.

Reactor based on the above design step is fabricated at the workshop of the FCIPT division, Institute for plasma research.

Fig (2): Reactor three dimensional drawing

Fig (3): Reactor plate three dimensional views

Reactor three dimensional drawing and its specification drawing is shown in figure 1, 2 and 3 respectively.

Catalyst used for decomposition of hydrocarbon into hydrogen is Ni catalyst found to contain 75 % of Ni as measured by X-ray analysis.
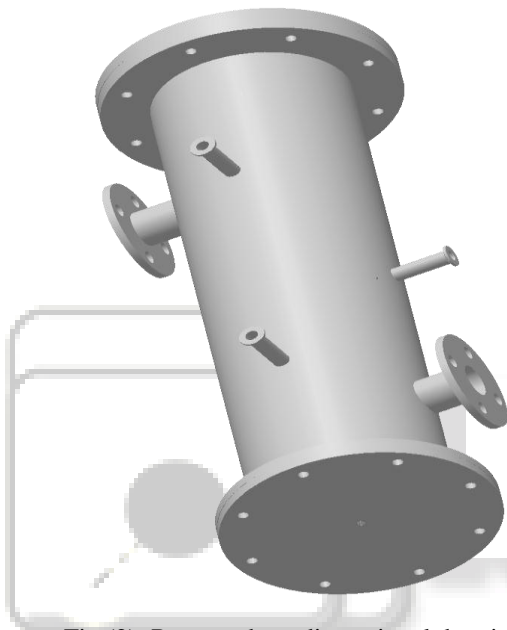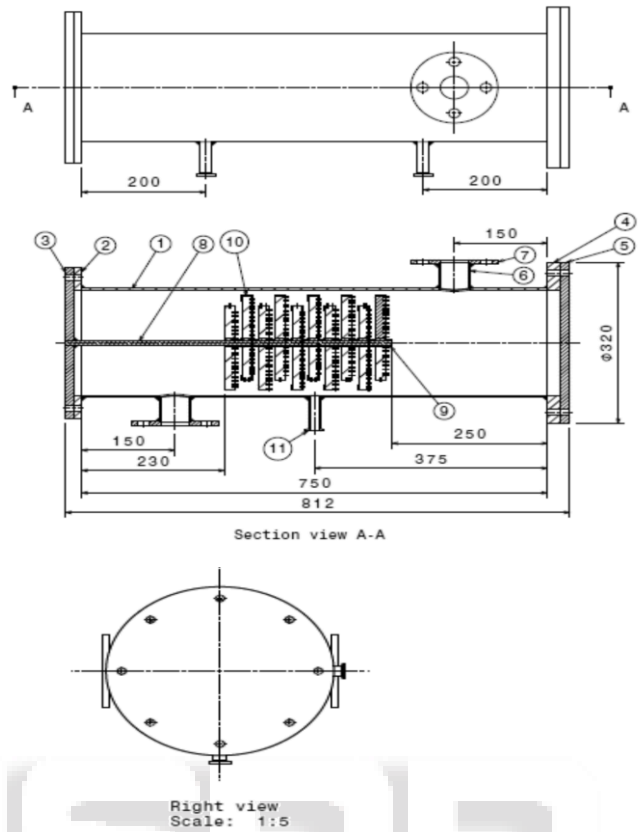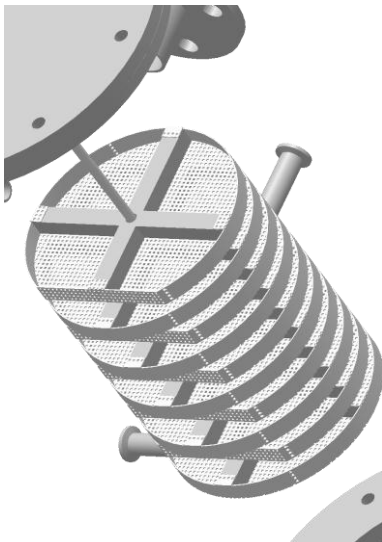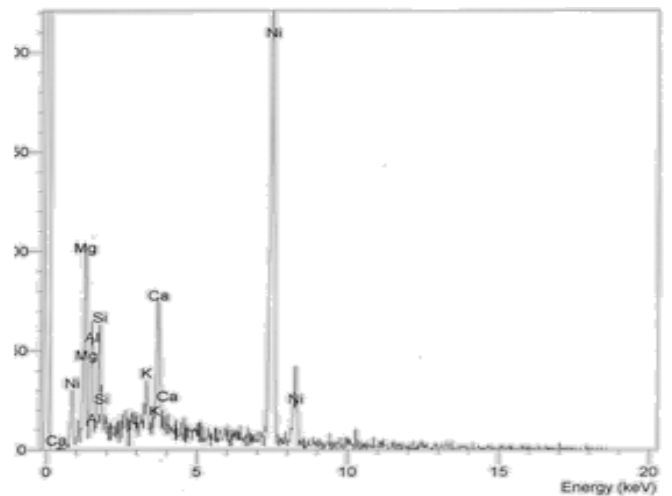

Section view A-A

Right view
Scale: 1:5

SL. NO	Description	Qty.	Material	Remarks
			-	-
11	16 KF COUPLER	3	MS	-
10	catalytic assy.	10	MS	-
09	spacer	10	MS	-
08	rod	1	SS	-
07	flange-5	2	MS	-
06	pipe-2	2	MS	-
05	flange-1	1	MS	-
04	flange-2	1	MS	-
03	flange-4	1	MS	-
02	flange-3	1	MS	-
01	pipe-1	1	MS	-

Fig (4): Reactor design specification.

Elmt	Spect. Type	Inten. Corrn.	Std Corrn.	Element %	Sigma %	Atomic %
Mg K	ED	0.486	0.64	15.93	1.00	29.15
Al K	ED	0.521	0.77	5.42	0.65	8.94
Si K	ED	0.610	0.93	2.83	0.45	4.48
Ni K	ED	0.954	1.00	75.81	1.24	57.43
Total				100.00		100.00

Fig (5): x ray analysis of Ni catalyst
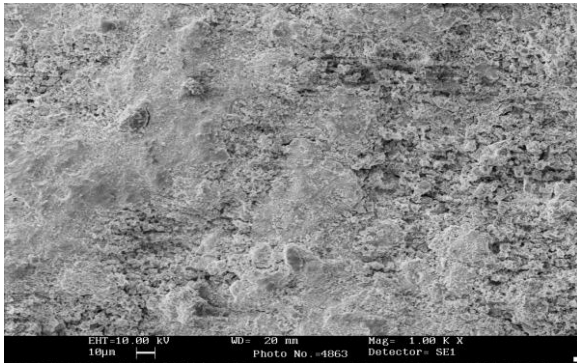
SEM analysis of Ni catalyst is shown below.

Fig (6)

IV. CONCLUSION

Ni catalysis loaded packed bed reactor can be used to maximize hydrogen generation from Ni catalyst. Vacuum residue feed flow rate, Primary pyrolysis chamber temperature, and pressure play important role in conversion of hydrocarbon to hydrogen. By varying flow rate at given temperature and pressure for a fixed catalyst weight followed by measuring gas concentration at inlet and outlet of reactor is useful to identify kinetics of the reaction as well as to optimize the given reactor. Similarly by changing temperature at constant pressure, volumetric flow rate and fixed catalyst weight we can find the conversion as well as effect of temperature on the conversion.

A. *Nomenclature*

$F_{i,0}$ = Molar flow rate of component i at reactor inlet.
F_i = Molar flow rate of component I at the reactor outlet.,
$C_{i,0}$ = Concentration of component I at reactor inlet.
C_i = Concentration of component I at reactor outlet.
τ = space time
$\upsilon_{i,0}$ = Volumetric flow rate of ith component at reactor inlet.
υ_i = Volumetric flow rate of ith component at reactor outlet.
$T_{,0}$ = Temperature at reactor inlet.
T= Temperature at reactor outlet.
$P_{,0}$= Pressure at reactor inlet.
P = Pressure at reactor outlet.
Z= Compressibility factor.
P_c = Critical pressure
P_r = Reduced pressure.
T_c= Critical temperature.
T_r = Reduced temperature.
ω= eccentricity factor.
R = Universal gas constant.
X= Conversion
δ_i = stoichiometric coefficient difference.

ε_i = Factional change in volume of gas per mole of ith component reacted.

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