World Journal of Engineering and Technology, 2015, 3, 18-25
Published Online October 2015 in SciRes. http://www.scirp.org/journal/wjet
http://dx.doi.org/10.4236/wjet.2015.33C003

Potential Cracking in Hydrogen Plant with Light Feedstocks (Part II)

Guotai Zhang, Sanjeev Sekhri

Process Department, Technip Stone & Webster Process, Technology Inc., Claremont, USA
Email: gzhang@technip.com, ssekhri@technip.com

Received 2 June 2015; accepted 15 October 2015; published 22 October 2015

Abstract

This paper presents the analysis of potential thermal cracking of light feedstocks in the SMR. Two different feedstocks, natural gas and light hydrocarbon (HC) feedstock at two different mixed feed inlet temperatures, are selected to study the HC thermal cracking. Effect of Crossover Piping Volume on feed thermal cracking is also discussed.

Keywords

Steam-Methane Reformer (SMR), Temperature Index (TI), Mixed Feed Preheater (MFPH), Crossover Piping Volume (CPV), Hydrocarbon (HC) and Thermal Cracking Kinetics

1. Introduction

H_2 can be produced from a variety of HC's, ranging from natural gas (methane) to petroleum-based gases and liquids. In our previous paper (Part I), we had quantitatively discussed thermal cracking of Liquefied Natural Gas (LNG), C_4 stream and naphtha feed stocks in the CPV of reformer [1] [2].

Parameters that affect thermal cracking are HC feed composition and component structure, mixed feed (HC + Steam) reformer inlet temperature and pressure, Steam/C mole ratio and mixed feed residence time in the CPV, etc. [3].

Natural gas is an important feed stock for SMR, however it is not a commodity with uniform composition and it includes N_2, CO_2, CH_4 and non-methane HC's.

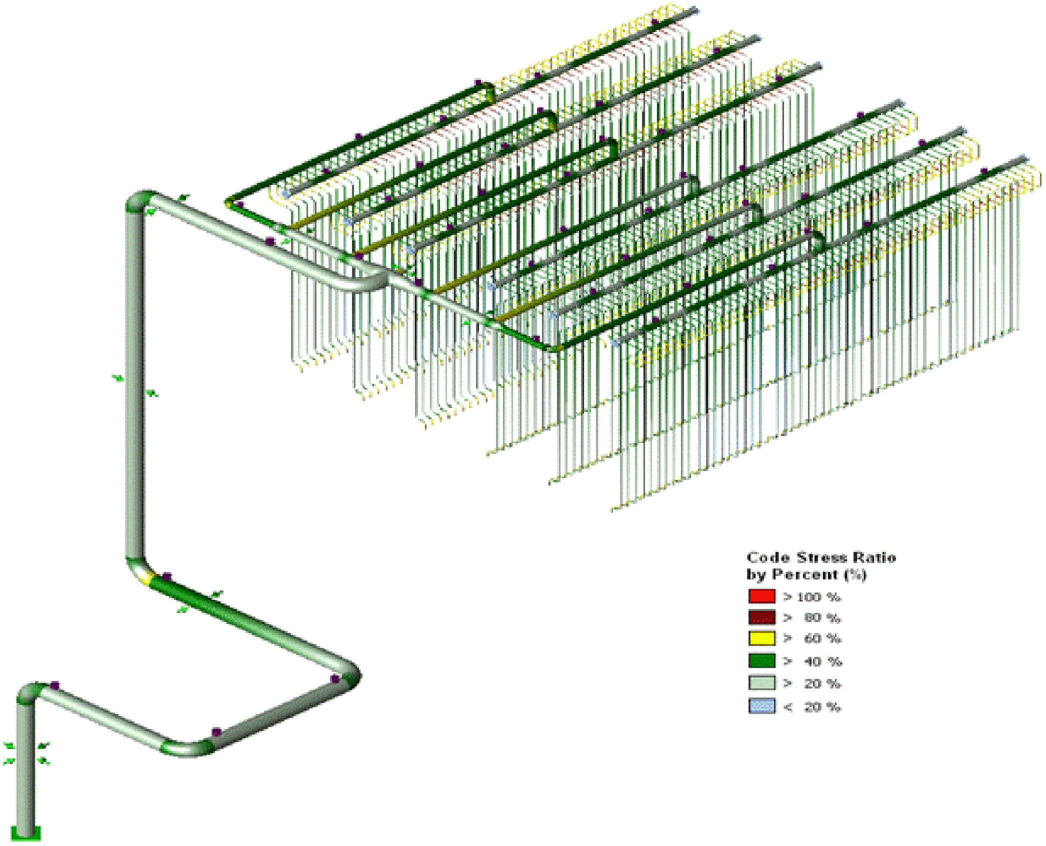
The objective of this study is to explore the parameters which will affect the undesired cracking of reformer feed stocks in the Mixed Feed Preheater (MFPH) coil and in the CPV. The parameters being considered are the mixed feed inlet temperature to the reformer and the residence time of mixed feed in the CPV. Also in this paper we introduce the concept of Temperature Index (TI) to indicate the thermal cracking potential of HC's.

HC feed is mixed with process steam and this stream is called mixed feed. The mixed feed is preheated in the MFPH Coil located in the convection section, and the preheated mixed feed is sent to the catalyst tubes through crossover piping (**Figure 1**).

2. Basis of Analysis

1) Scope

How to cite this paper: Zhang, G.T. and Sekhri, S. (2015) Potential Cracking in Hydrogen Plant with Light Feedstocks (Part II). *World Journal of Engineering and Technology*, **3**, 18-25. http://dx.doi.org/10.4236/wjet.2015.33C003



(a) (b)

Figure 1. Typical layout of crossover piping. (a) MFPH coil outlet from convection section; (b) To catalyst tubes in SMR.

This paper analyses potential of thermal cracking in the MFPH Coil and crossover piping from MFPH coil outlet to the inlet of SMR.

2) MFPH Coil

MFPH Coil geometry and tube material are listed below (**Table 1**) which are used in the simulation for all cases.

3) Feed Composition

Case 1 feed (Natural Gas) has N_2, CO_2, CH_4 and non-methane hydrocarbons as shown in **Table 2**. The feed inlet temperature to the reformer is relative low.

Case 2 is a light feed which is treated in the pre-reformer. It has more H_2 and CO_2, CH_4 and no C_2 + hydrocarbons as shown in **Table 3**. The feed inlet temperature to the reformer can be relative high.

Table 4 and **Table 5** below are the Mixed Feed Preheater Coil (MFPH) design bases for process gas and flue gas.

4) Crossover Piping Volume (CPV)

Assume CPV is an adiabatic zone with no heat loss. CPV is constant for all cases which is 24.7 m^3 per SMR.

5) Pressure Drop

Assume 0.35 kg/cm^2 drop through CPV.

3. Design Tool-SPYRO® Program

The SMR feedstock cracking kinetics has been simulated using SPYRO® program which is widely used by the industry for prediction of hydrocarbon cracking.

SPYRO® is a unique program for prediction of cracking furnace effluent yields as well as overall performance of the furnace. SPYRO® is the only program which is based on the rigorous fundamental mathematical equations

Table 1. MFPH coil specification.

MFPH # of Rows	Tube Size NPS	Hori/Vert Distance inch	Tubes per Row	No. of Passes	Tube Material
8 (outlet)	3” Sch 80	8/6	14	28	**800H**
7	3” Sch 80	8/6	14	28	
6	3” Sch 80	8/6	14	28	
5	3” Sch 40	8/6	14	28	
4	3” Sch 40	8/6	14	28	
3	3” Sch 40	8/6	14	28	
2	3” Sch 80	8/6	14	28	
1 (inlet)	3” Sch 80	8/6	14	28	

Note 1: Total 8 rows in MFPH coil. 2: Effective tube length 13.2 m for all tubes. 3: All tubes are bare. 4: Process gas and flue gas are in co-current flow.

Table 2. Case 1 feed composition.

Composition	MW	Mixed Feed	
		Mol %	Wt %
H_2	2.0159	0.85	0.097
N_2	28.014	0.55	0.874
CO_2	44.01	0.49	1.224
CH_4	16.043	26.00	23.669
C_2H_6	30.07	0.38	0.648
C_3H_8	44.097	0.05	0.125
iC_4H_{10}	58.124	0.01	0.033
nC_4H_{10}	58.124	0.01	0.033
nC_6H_{14}	86.177	0.01	0.049
H_2O	18.015	71.65	73.247
Total		100.00	100.000
MW	Kg/Mol	17.623	
Steam/C	Mol/Mol	2.65	

Table 3. Case 2 feed composition.

Composition	MW	Mixed Feed	
		Mol %	Wt %
H_2	2.0159	7.25	0.86
N_2	28.014	0.57	0.94
CO	28.01	0.04	0.07
CO_2	44.01	2.22	5.75
CH_4	16.043	26.23	24.79
H_2O	18.015	63.69	67.59
Total		100.00	100.000
MW	Kg/Mol	16.976	
Steam/C	Mol/Mol	2.42	

Table 4. MFPH coil design basis (process gas data).

	Units	Case 1		Case 2	
		MFPH Inlet Stream			
Pressure	Kg/cm^2-a	39.4		39.3	
Temp.	°C	368.4		456.4	
Flow	Kmol/h	7,212		6,557	
		MFPH Outlet and Reformer Inlet Streams			
		MFPH Outlet	**SMR Inlet**	**MFPH Outlet**	**SMR Inlet**
Pressure	Kg/cm^2-a	38.4	38.0	38.3	37.9
Temp.	˚C	593.5	593.3	649.3	648.9
Resid.Time in CPV	Sec	6.4		6.6	

Table 5. MFPH design basis (flue gas data).

	Units	Case 1	Case 2
Flue Gas			
Pressure	Kg/cm^2-a	1.0	1.0
Temperature	˚C	1003	1001
Flow	Kmol/h	10,540	9310
Composition	Mol %		
CO_2		19.15	20.54
Ar		0.73	0.71
O_2		1.63	1.45
N_2		61.59	59.84
H_2O		16.90	17.46
Total		100.00	100.00

representing reaction kinetics of almost all chemical, thermo-chemical reactions in the pyrolysis furnace.

SPYRO® is now used by more than 85% of the ethylene producing industry worldwide. The latest program version and kinetic model SPYRO®-7 covers all hydrocarbon species from C2 to C42 and more than 7000 reactions. This version also allows better flexibility in establishing the furnace and heat recovery flowsheet.

4. Fundamentals of Thermal Cracking

For the sake of completeness, we are recapping the fundamentals of thermal cracking from paper Part I (1) in this section [4].

1) Bond Energy

Bond energy is a measure of bond strength in a chemical bond. The larger the bond energy, the stronger the bond and hence the higher temperature required to break it. The bond energy is essentially the average enthalpy change for a gas reaction to break all the similar bonds. For the methane molecule, CH_3-H, 104 kcal is required to break the first single C-H bond for a mole of methane, but breaking all four C-H bonds for a mole of methane requires 397 kcal. Thus, the average bond energy is (397/4) 99 (not 104) kcal/mol.

2) Bond Length

Distance between centers of bounded atoms is called bond length. There is a general trend in that the shorter the bond length, the higher the bond energy. Some typical bond lengths and bond energies are given below to illustrate a general trend (**Table 6** and **Table 7**).

Table 6. Bond length and bond energy.

Bond Type	Bond Length Picometer (pm), 1 pm = 10^{-12} m	Bond Energy Kcal/mol
H-H	74	104
H-C	109	99
C-C	154	83
C=C	134	147
C≡C	120	200

Table 7. Bond energy of chemicals, Kcal/mol.

Atom or Group	H	CH_3	C_2H_5	$(CH_3)_2CH$	$(CH_3)_3C$	C_6H_5	$C_6H_5CH_2$
H	104	103	98	95	93	110	85
CH_3	103	88	85	84	81	101	73
C_2H_5	98	85	82	81	78	99	71
$(CH_3)_2CH$	95	84	81	79	74	97	70
$(CH_3)_3C$	93	81	78	74	68	94	67
C_6H_5	110	101	99	97	94	110	83
$C_6H_5CH_2$	85	73	71	70	67	83	59

CH_3: -methyl: C_2H_5: -ethyl:$(CH_3)_2CH$: i-propyl $(CH_3)_3C$: -t-butyl C_6H_5: -phenyl $C_6H_5CH_2$: -benzyl.

3) Temperature Index

Temperature Index (TI) represents the mixed feed temperature reduction due to the thermal cracking and chemical reaction in the adiabatic zone *i.e.* crossover piping volume (CPV).

4) General Cracking Rules

a) Bond energy comparison between different atoms

H-H > C-H > C-C (C-C is easier to break)

b) Dehydrogenation ability of HC depends upon its structure and is in the order of:

Tertiary H > Secondary H > Primary H

c) For carbon-carbon bonds, the order of bond energy:

Triple Bond > Double Bond > Single Bond

d) Order of heat stability for paraffin is:

$CH_4 > C_2H_6 > C_3H_8 > C_4H_{10} >$

e) For HC with same C atoms, heat stability order is:

Aromatics > Naphthene > Di-Olefin > Olefin > Paraffin

5. Simulation Results

1) Effect of feed composition and mixed feed inlet temperature on the thermal cracking and MFPH coil material selection.

Data in **Table 8** indicates there are three different reactions in the MFPH coil and CPV for Case 1 feed.

a) Steam-HC reforming reactions which are irreversible reactions at normal condition.

b) Methane reacts with water steam to form carbon monoxide and hydrogen (the mixture of CO and H_2 is known as syngas), which is a reversible chemical reaction, $CH_4 + H_2O \rightleftharpoons CO + 3H_2$.

c) Water-gas shift reaction (WGSR) is a reversible chemical reaction in which carbon monoxide reacts with water vapor to form carbon dioxide and hydrogen, $CO + H_2O \rightleftharpoons CO_2 + H_2$.

Table 9 shows there is no thermal cracking for Case 2 feed because methane is stable and there are no non-methane hydrocarbons, such as ethane, propane, etc in the feed.

However, Reverse Water-Gas Shift (RWGS) reaction, $CO_2 + H_2 \rightarrow CO + H_2O$, which is an endothermic reaction, can be involved in both MFPH coil and crossover piping volume as shown in **Table 9**.

Table 8. Case 1 Stream composition at different locations.

Location	Mixed Feed to MFPH	MFPH Outlet	Outlet of Cross Over Piping
Mixed FeedFlow, Kg/h	127,097	127,097	127,097
	Composition mol% (wet)		
Hydrogen	0.8500	0.8499758	0.8512
Methane	26.0000	25.9999995	25.9998
Ethylene	**-**	**0.0000045**	**0.0031**
Ethane	0.3800	0.3799983	0.3791
Propylene	**-**	**0.0000020**	**0.0015**
Propane	0.0500	0.0499983	0.0487
Butenes	**-**	**0.0000008**	**0.0004**
Butanes	0.0200	0.0199987	0.0190
n-Hexane	0.0100	0.0099988	0.0092
1-Pentene	**-**	**0.0000001**	**0.0001**
Carbon Monoxide	-	0.0000286	0.0017
Carbon Dioxide	0.4900	0.4899714	0.4883
Nitrogen	0.5500	0.5500000	0.5500
Water	71.6500	71.6500230	71.6478
Total	100.0000	99.9999998	100.0000
Total Olefins	**-**	**0.0000074**	**0.0051**
Temperature ˚C	**368.4**	**593.5**	**593.3**

Table 9. Case 2 stream composition at different locations.

Location	Mixed Feed to MFPH	MFPH Outlet	Outlet of Cross Over Piping
Mixed FeedFlow, Kg/h	111,312	111,312	111,312
	Composition mol% (wet)		
Hydrogen	**7.25**	**7.2464**	**7.1864**
Methane	26.23	26.2300	26.2300
Carbon Monoxide	**0.04**	**0.0436**	**0.1036**
Carbon Dioxide	**2.22**	**2.2164**	**2.1564**
Nitrogen	0.57	0.5700	0.5700
Water	**63.69**	**63.6936**	**63.7536**
Total	100.00	100.0000	100.0000
Temperature ˚C	**456.4**	**649.3**	**648.9**

Table 10 and **Table 11** list the maximum tubewall temperature profiles for Cases 1 and 2, respectively.

2) Effect of crossover piping volume on cracking

The effect of SMR crossover piping volume on the mixed feed thermal cracking is shown in **Figure 2**. Case 1 feed is used for the study.

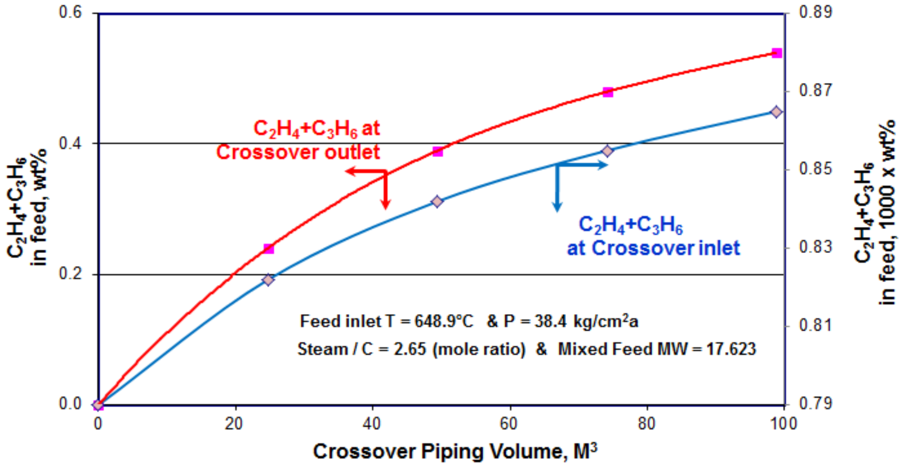


Figure 2. Effect of CPV on case 1 feed thermal cracking.

Table 10. Case 1 MFPH max tubewall temperature (MTT).

No. of Rows	Case 1				
	Mixed Feed Temp, ˚C	Flue Gas Temp. ˚C	Simulation MTT, ˚C	Design Temp, ˚C	Material
Row 8	593.5 (outlet)	821.7 (outlet)	646.7	743.9	800H Sch 80
Row 7			633.9		
Row 6			616.1		
Row 5			643.3	693.9	800H Sch 40
Row 4			596.1		
Row 3			556.1		
Row 2			614.4	743.9	800H Sch 80
Row 1	368.4 (inlet)	1003.3 (inlet)	612.2		

Table 11. Case 2 MFPH max tubewall temperature (MTT).

No. of Rows	Case 2				
	Mixed Feed Temp, ˚C	Flue Gas Temp. ˚C	Simulation MTT, ˚C	Design Temp, ˚C	Material
Row 8	649.3 (outlet)	842.2 (outlet)	689.4	743.9	800H Sch 80
Row 7			678.3		
Row 6			663.3		
Row 5			640.0	693.9	800H Sch 40
Row 4			645.0		
Row 3			611.7		
Row 2			661.1	743.9	800H Sch 80
Row 1	456.4 (inlet)	1001.1 (inlet)	661.7		

For constant mixed feed flowrate, the residence time of mixed feed in the crossover piping is decided by the crossover piping volume, which depends on the crossover piping dimension and the distance from convection section outlet (Point A in **Figure 1**) to the reformer inlet location (Point B in **Figure 1**).

Table 12 shows that the larger CPV will have the longer residence time and hence the more light olefins ($C_2H_4 + C_3H_6$) formed in CPV.

Table 12. Effect of CPV on Case 1 feed cracking.

Mixed feed flowrate, kg/h	127,090 (Case 1)				
Crossover Piping Volume (CPV), m^3	0.0	24.7	49.4	74.1	98.8
MFPH outlet temperature, ˚C	**648.9**	**649.9**	**650.5**	**650.9**	**651.2**
Residence time in CPV, sec	0.0	6.0	12.0	18.0	24.0
Mixed feed T drop in CPV, ˚C	**0.0**	**−1.0**	**−1.6**	**−2.0**	**−2.27**
Mixed feed T at SMR inlet, ˚C	**648.9**	**648.9**	**648.9**	**648.9**	**648.9**
$C_2H_4 + C_3H_6$ at MFPH outlet, wt% (dry)	7.90E−4	8.22E−4	8.42E−4	8.55E−4	8.65E−4
$C_2H_4 + C_3H_6$ formed in CPV, wt% (dry)	0.0	0.239	0.389	0.479	0.539
$C_2H_4 + C_3H_6$ at SMR inlet, wt% (dry)	**7.90E−4**	**0.24**	**0.39**	**0.48**	**0.54**

Therefore, it is better to keep the CPV as small as possible to avoid higher light olefins entering into the reformer.

The mixed feed temperature at the reformer inlet is equal to the MFPH feed outlet temperature minus the mixed feed temperature drop in the crossover piping volume.

6. Conclusions

1) There is not only thermal cracking but also chemical reaction in the MFPH coil and crossover piping volume which is an adiabatic zone.

2) There is a slight thermal cracking and chemical reactions in both MFPH coil and crossover volume for Case 1 and Temperature Index (TI) is 0.2˚C.

3) There is no thermal cracking for Case 2 feed because of non-methane hydrocarbons in the feed. However, Reverse Water-Gas Shift (RWGS) reaction, which is an endothermic reaction, can be involved in both MFPH coil and crossover volume. Hydrogen reacts with carbon dioxide to form carbon monoxide and water vapor and TI is 0.4˚C.

4) Larger Crossover Piping Volume results in a higher temperature reduction in the adiabatic zone and therefore, more light olefins to the reformer and easy to form coke in reformer tubes.

5) Maximum tubewall temperature profiles for MFPH coil are useful to select the correct tube material.

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